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Selectivity of gas phase adsorption of propene and propane onto mesoporous silica materials derivatised with Ag(I) and Cu(II) at low surface coverages: comparison between equilibrium adsorption and flow microcalorimetry studies

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Abstract

Adsorption selectivity for propene over propane of mesoporous aluminosilicate monoliths derivatised with Ag(I) and Cu(II) has been studied from the gas phase at low surface coverages at 298 K. The insertion of transition metals was achieved by ion exchange, incipient wetness impregnation or direct incorporation during the synthesis stage. The overall transition metal content in the samples ranged between 2 and 20 wt.%. Two-cycle adsorption of each gas measured at pressures up to 300 mbar was used to determine the reversible and irreversible contributions to the amount adsorbed under equilibrium conditions. Flow microcalorimetry measurements allowed estimates of the reversible and irreversible enthalpy components to be made under flow conditions. Adsorption selectivity of the derivatised aluminosilicates changes when passing from one adsorption system to another. Both Ag(I) and Cu(II) can give selective adsorption of propene over propane under experimental conditions close to the adsorption equilibrium, whereas only Ag-containing samples are selective under flow conditions.

Keywords: Adsorption of propane and propene; Mesoporous silica materials; Derivatisation with Ag(I) and Cu(II); Adsorption reversibility; Flow microcalorimetry

1. Introduction

There has been much evidence that solids derivatised with transition metal cations such as silver and copper can be used in separation of gaseous alkene–alkane mixtures [1–7]. The selectivity of such adsorbent preparations is commonly derived from the propensity of metal ion sites to preferentially bind unsaturated alkene molecules through π donor–acceptor type interactions, whereas saturated hydrocarbons are only physisorbed on the solid surface. In order to maximise this selectivity, it is necessary to control, on the one hand, the surface properties and porosity of the adsorbent and, on the other hand, the metal content, its oxidation state and dispersion over the surface. Several steps in the preparation procedure including the synthesis route used to prepare the supporting solid phase and the method of metal addition may affect the selective adsorption of alkenes towards alkanes.

Recently, Cu(II) and Ag(I) derivatised aluminosilicate monoliths possessing high internal surface area and uniformly sized mesopores were synthesised via the direct liquid crystal templating pathway to obtain shaped materials for the selective adsorption of propene against propane [8]. The insertion of a transition metal was achieved by ion exchange from metal nitrates in solution, incipient wetness impregnation or a sol–gel synthesis of silica in the presence of a given metal nitrate, also called direct incorporation. Several shaped aluminosilicates derivatised with different amounts

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of metal were prepared. Depending on the method of metal addition and the overall metal content in the sample, metal ions and/or metal oxides are more or less highly dispersed over the supporting surface. The suitability of the prepared adsorbent formulations for selective alkene–alkane adsorption was assessed on the basis of the individual adsorption of propene and propane from the gas phase in an equilibrium pressure range from 25 to 1013 mbar. Generally, the highest adsorption capacity ratio for propene over propane was attained at low equilibrium pressures.

The intention of the present study was to shed light on the adsorption selectivity under experimental conditions corresponding to the most promising applications of monolithic aluminosilicate adsorbents. A vacuum-pressure swing adsorption process is one of the possible uses, where the adsorbent bed is cycled from adsorption to desorption by changing the pressure inside the adsorbent vessel. Here the processing conditions correspond practically to the adsorption equilibrium. The monolithic aluminosilicates may be also formulated to act as membranes under flow conditions to ensure continuous gas supply. In this case, the adsorption system is rather far from the adsorption equilibrium. The adsorption of propane and propene was studied at low surface coverages, where the chemisorption of unsaturated molecules was expected to mostly contribute to the adsorption phenomenon, the propane molecules being rather physisorbed. A two-cycle adsorption procedure was used first to quantify the reversible and irreversible contributions to the amount adsorbed under equilibrium conditions. Then, flow microcalorimetry measurements allowed determination of the molar enthalpy of adsorption and estimates of the reversible and irreversible enthalpy components. The experimental results reveal some important differences in the adsorption selectivity for both gases under static and flow conditions, that depend upon the nature and content of the metal in the sample.

2. Experimental

2.1. Materials

A typical synthesis of the shaped aluminosilicates following the direct liquid crystal templating pathway in high-concentration surfactant solution and acidic medium is described in [9]. The synthesis and modification routes leading to the derivatised monoliths are detailed in [8]. The calcined samples used in the present study are crack-free cylindrical samples of ca. 2 mm in diameter and their length ranges between 3 and 5 mm. The Si:Al molar ratio is 20, and the samples are further referred to as SiAl20. The functionalised aluminosilicates are designated SiAl20MX, where M denotes the added metal (M = Cu or Ag) and X is the metal content in the final sample (wt.%). An additional subscript is used to distinguish amongst the samples obtained by different methods of metal addition: EX, IM and DI referring to, respectively, ion exchange, impregnation and direct incorporation. The adsorbent containing 10 wt.% of Cu obtained by impregnation of SiAl20 with copper nitrate is thus designated $\text{SiAl20Cu10}_{\text{IM}}$. The cylindrically shaped aluminosilicates derivatised with metal nitrates by impregnation and ion exchange were only dried after metal addition. For each adsorbent sample, the specific surface area and the mean pore size were determined from nitrogen gas adsorption measurements at 77 K using BET analysis and the improved MP method [8]. These parameters are collected in Tables 1 and 2.

Gaseous helium, propane and propene of ultra high purity were purchased from Air Liquide (France).

2.2. Methods

The individual adsorption of propane and propene from gas phase at 298 K was studied using a Micromeritics ASAP 2010 apparatus. A solid sample of ca. 150 mg was placed in a glass cell and outgassed overnight at 423 K. Then it was cooled down to 298 K in a flow of helium. During adsorption measurements, successive doses of the reactive gas (propene or propane) were sent onto the sample until a given equilibrium pressure was reached. The amount adsorbed was determined after each adsorption step. The adsorption procedure was continued up to an equilibrium pressure of about 300 mbar. At the end of the first adsorption cycle, the sample was outgassed under vacuum at 298 K for 30 min and a second adsorption cycle was performed in the same pressure range and at the same temperature.

A flow calorimetric study of gas hydrocarbon adsorption at 298 K was carried out with the use of a 4Vms Microscal flow microcalorimeter [10] equipped with a loop injection facility (a Valco P series valve with a 50 μL injection loop). The pulse technique allowed introduction of a defined volume of the pure reactive gas (propane or propene) by injection into the carrier gas flowing through the adsorbent bed. The progress of adsorption was continuously monitored by the evolution of heat measured by thermistors sensing temperature changes in the adsorbent bed and simultaneously adsorbate transfer from the gas phase to the solid–gas interface was monitored by measuring composition changes in the effluent leaving the calorimetric cell and passing through an on-line thermal conductivity (TC) detector. Prior to measurement, the solid sample was gently crushed to decrease the dead volume of the adsorbent bed, placed in the calorimetric cell, outgassed at 298 K overnight, and subsequently flushed with a helium flow of 2 ml min^{-1} for 2 h. Three successive injections of 2 μmol of propane or propene were made, using the loop injection system. Each gas dose was brought into contact with the solid surface, giving rise to a positive heat effect. For some adsorption systems, heat evolution ceased after about 15 min and the signal returned to its baseline. No changes in the thermal conductivity of the effluent were recorded, indicating the irreversible adsorption of the adsorbate. In other cases, the initial positive heat effect was followed by a negative one indicating the desorption of the adsorbate from the solid surface by the carrier gas stream. The corresponding changes

Table 1
BET specific surface area, S_{BET}, mean pore diameter, d_p, amount of Cu incorporated per unit mass of the derivatised sample and the irreversible contribution to the quantity of propene adsorption, n_{IR}^{a}, for the Cu-containing aluminosilicate monoliths

Sample	S_{BET} ($m^2 g^{-1}$)	d_p (nm)	Cu content ($mmol\,g^{-1}$)	n_{IR}^{a} ($mmol\,g^{-1}$)	n_{IR}^{a} ($\mu mol\,m^{-2}$)
$SiAl20Cu7_{EX}$	384	2.9	1.1	0.12	0.32
$SiAl20Cu2_{IM}$	848	2.6	0.31	0.26	0.31
$SiAl20Cu5_{IM}$	871	2.9	0.79	0.15	0.17
$SiAl20Cu10_{IM}$	489	3.0	1.57	0.20	0.41
$SiAl20Cu20_{IM}$	454	2.7	3.15	0.25	0.55
$SiAl20Cu2_{DI}$	784	2.2	0.31	0.62	0.79
$SiAl20Cu5_{DI}$	813	2.3	0.79	0.32	0.39
$SiAl20Cu10_{DI}$	960	2.2	1.57	0.22	0.23
$SiAl20Cu20_{DI}$	875	2.7	3.15	0.16	0.18

Table 2
BET specific surface area, S_{BET}, mean pore diameter, d_p, amount of Ag incorporated per unit mass of the derivatised sample and the irreversible contribution to the quantity of propene adsorption, n_{IR}^{a}, for the Ag-containing aluminosilicate monoliths

Sample	S_{BET} ($m^2 g^{-1}$)	d_p (nm)	Ag content ($mmol\,g^{-1}$)	n_{IR}^{a} ($mmol\,g^{-1}$)	n_{IR}^{a} ($\mu mol\,m^{-2}$)
$SiAl20Ag20_{EX}$	258	3.9	1.85	0.18	0.70
$SiAl20Ag2_{IM}$	917	2.4	0.18	0.21	0.23
$SiAl20Ag5_{IM}$	927	2.7	0.46	0.23	0.25
$SiAl20Ag10_{IM}$	603	2.4	0.93	0.23	0.38
$SiAl20Ag20_{IM}$	577	2.6	1.85	0.34	0.59
$SiAl20Ag2_{DI}$	909	2.1	0.18	0.44	0.48
$SiAl20Ag5_{DI}$	890	2.2	0.46	0.17	0.19
$SiAl20Ag10_{DI}$	841	2.2	0.93	0.17	0.20
$SiAl20Ag20_{DI}$	585	2.4	1.85	0.18	0.31

in the thermal conductivity of the effluent were recorded in the form of a desorption peak. Calibration of the areas under the thermal peaks was carried out by dissipating a known amount of energy in the cell under the same flowing conditions (Joule heating using a calibration probe incorporated into the outlet tube) and integrating the related exothermic peak. The TC detector calibration factor was determined from the injection of 50 μL of pure propane or propene into the stream of helium carrier gas percolating through the detector.

3. Results

3.1. Two-cycle adsorption of propane and propene

Equilibrium adsorption studies provide two adsorption isotherms corresponding to the amounts of propane or propene adsorbed in two successive adsorption cycles at various equilibrium pressures. In the case of propane, the two adsorption curves superimpose over the pressure range studied (up to 300 mbar). This indicates that all propane molecules adsorbed in the first cycle of adsorption can be easily removed during 30 min of pumping. The adsorption of propane is thus completely reversible under batch conditions. Figs. 1 and 2 therefore show a single isotherm of propane adsorption for several selected aluminosilicate samples derivatised with similar amounts of copper or silver by different methods of metal addition, while for propene, there is a difference between the two adsorption isotherms. Pumping is not sufficient to remove the whole gas adsorbed, since some propene molecules are irreversibly retained at the solid–gas surface. The adsorption difference between the two cycles appears a constant function of the equilibrium pressure in most of the adsorption systems. The examples of such a curve are shown in Figs. 1 and 2. In consequence, the second-cycle isotherm may be ascribed to the reversible adsorption of propene on the solid surface, whereas the difference between the two adsorption cycles gives the estimate of the irreversible contribution to the amount adsorbed. Only for $SiAl20Cu2_{DI}$ and $SiAl20Cu5_{DI}$, the adsorption difference slightly increases with increasing pressure up to 300 mbar. It may be that the active sites responsible for the irreversible adsorption of propene on these adsorbents are very heterogeneous. The molecules adsorbed in the first cycle on weakly active sites are probably removed during deep pumping at 298 K and subsequently re-adsorbed during the second cycle.

3.2. Adsorption of propane and propene under flow conditions

Flow microcalorimetry measurements allow the molar enthalpy of adsorption of a given gas component onto solid sample to be determined, thereby providing valuable information about the solid–adsorbate interaction. However, the direct interpretation of the calorimetric data may be quite difficult for some adsorption systems.

Fig. 3 shows a part of the typical trace for a pulse run obtained by injecting propene on $SiAl20Cu10_{DI}$. The heat

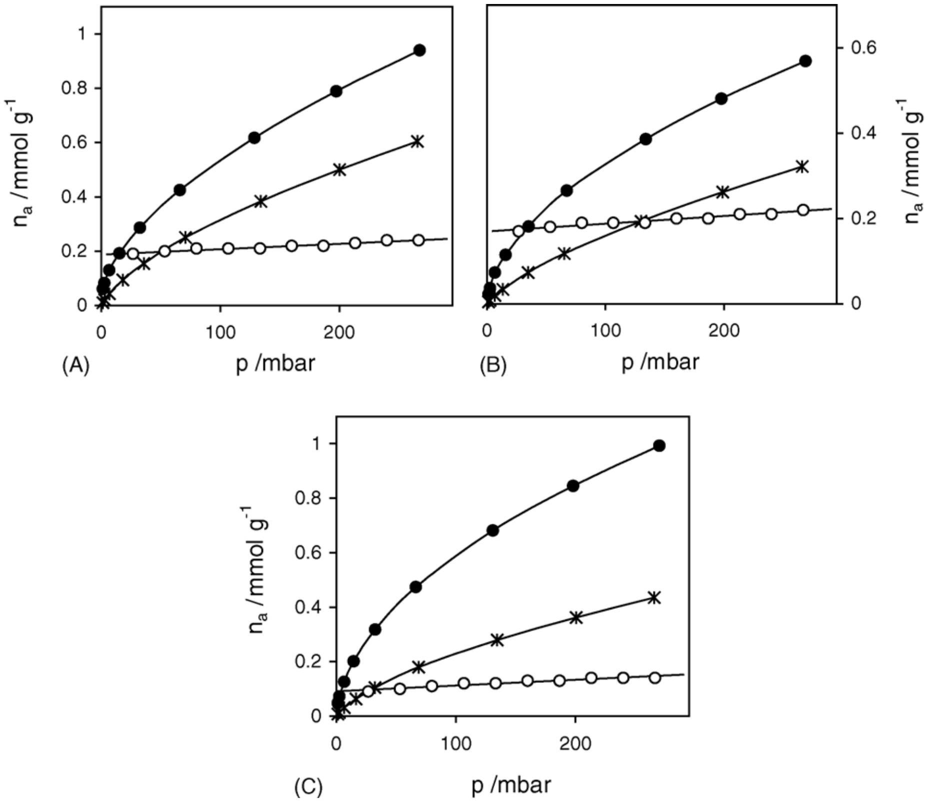

Fig. 1. Isotherms of propane (crosses) and propene (circles) adsorption at 298 K onto aluminosilicates derivatised with copper: (A) SiAl20Cu10$_{DI}$, (B) SiAl20Cu10$_{IM}$, (C) SiAl20Cu7$_{EX}$. For propene, the reversible (solid circles) and the irreversible (open circles) contributions to the amount adsorbed, n_a, are plotted against the equilibrium pressure, p.

effect corresponding to the injection step is composed of two parts, one of which represents a sharp exothermic peak and the other is a broad endothermic signal. The amount of C_3H_6 detected by the TCD detector in the gas flowing out from the calorimetric cell is equal to that initially injected into the carrier gas. The adsorption of propene is thus completely reversible. The thermal-channel output data in Fig. 3 should represent a sum of two equal heat contributions which differ only in sign: the first one corresponding to the 'instantaneous' adsorption of propene on the surface of the adsorbent and the other being characteristic of the gradual gas release from the surface under the action of flowing carrier gas. To determine the thermal effect of reversible adsorption, $\Delta_a H_R$, it is sufficient to calculate the area under the thermal profile in Fig. 3 and to divide it by 2. The resulting value of $\Delta_a H_R$ and the amount of propene injected into the calorimetric cell provide direct access to the molar enthalpy of reversible adsorption, $\Delta_a h_R$. This enthalpic value, averaged over three successive runs, corresponds to the mean integral enthalpy of propene adsorption on the solid surface flushed with the inert helium (Table 3).

Completely reversible adsorption of propane and propene was observed for all Cu-containing samples. The values of $\Delta_a h_R$ were calculated following the above described procedure and are reported in Tables 3 and 4. Completely irreversible adsorption of propene was detected on aluminosilicates modified with silver by all the three methods of metal addition. The molar enthalpy of irreversible adsorption, $\Delta_a H_{IR}$, was thus calculated by integrating the corresponding exothermic peak and dividing it by the amount of propene injected into the carrier gas, the latter quantity being identical to the amount of propene irreversibly adsorbed. Note that the molar enthalpy of propene adsorption onto SiAl20Cu7$_{EX}$ is missing in Table 3. Here the adsorption phenomenon under flow conditions was not completely reversible since the amount of propene desorbed was smaller than that injected initially into the calorimetric cell. Hence, it was not possible to separate the total thermal effect into the reversible and irreversible contributions.

4. Discussion

In Figs. 1 and 2, it is possible to define the pressure range in which the adsorption isotherm of propane lies below the curve of irreversible propene adsorption. This means that propene can be adsorbed selectively over propane in this interval. The length of the selectivity range and the selectivity ratio depend on the nature of the metal, its content, and the method by which it has been incorporated. In the case of materials containing ca. 10 wt.% of copper, the best selectivity is obtained on the impregnated sam-

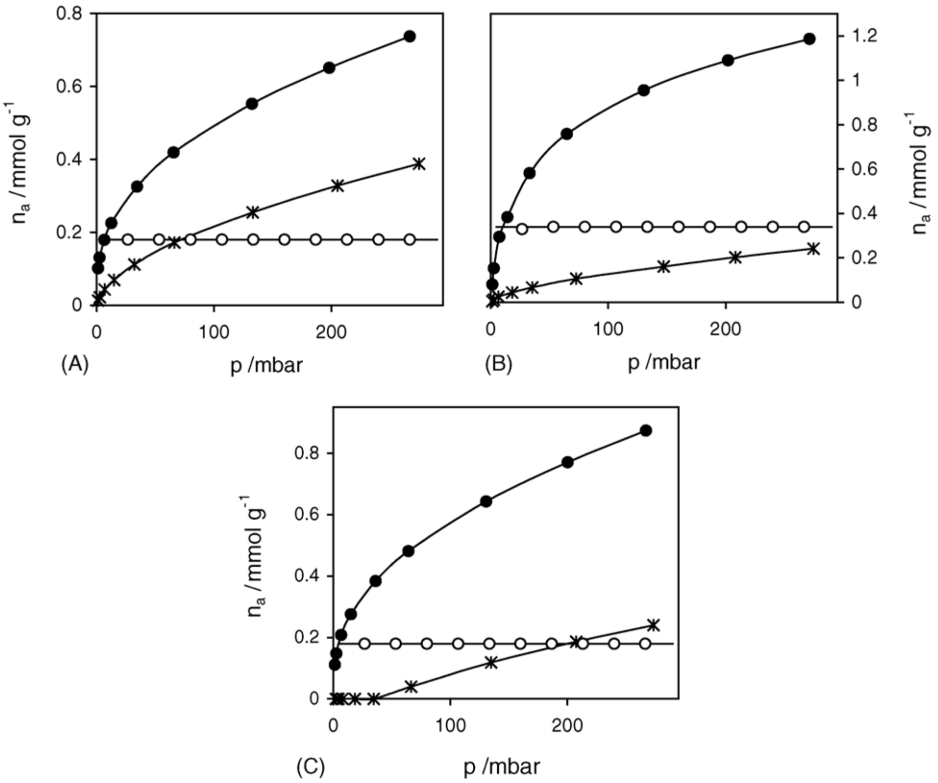

Fig. 2. Isotherms of propane (crosses) and propene (circles) adsorption at 298 K onto aluminosilicates derivatised with silver: (A) SiAl20Ag20$_{DI}$, (B) SiAl20Ag20$_{IM}$, (C) SiAl20Ag20$_{EX}$. For propene, the reversible (solid circles) and the irreversible (open circles) contributions to the amount adsorbed, n_a, are plotted against the equilibrium pressure, p.

ple. SiAl20Cu7$_{EX}$ is characterised by the lowest selectivity (i.e., the smallest irreversible adsorption of propene and the narrowest selectivity range). Amongst the samples with the highest silver loading, SiAl20Ag20$_{IM}$ selectively adsorbs propene against propane in the whole pressure range studied and the irreversible propene adsorption is almost twice that of the other samples. The ion-exchanged monolith exhibits a good selectivity in the range of very low equilibrium pressures where propane adsorption is practically to be neglected.

The irreversible contributions to the quantity of propene adsorption at the solid–gas interface, n^a_{IR}, expressed per unit mass or per unit surface area of the adsorbent are given in Tables 1 and 2. For the comparison purposes, the amount of transition metal contained in 1 g of the derivatised sample is also reported. The ion-exchanged samples contain Cu(II) and

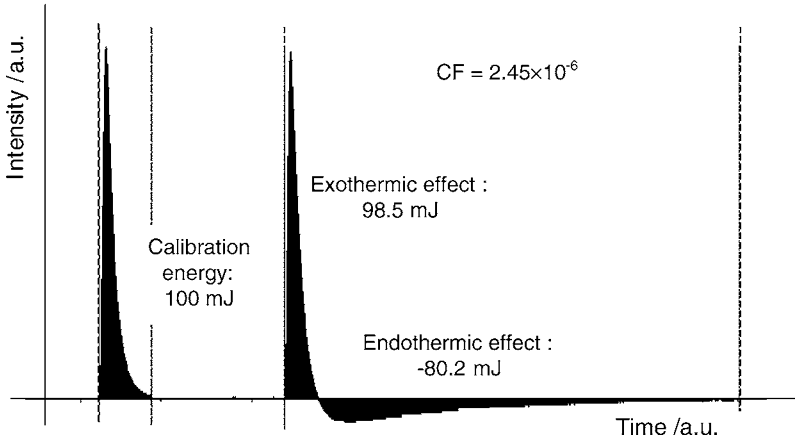

Fig. 3. Thermal–channel output data showing heat effects produced by a calibration and one injection of 2 μmol of propene on 0.117 g of SiAl20Cu10$_{DI}$. The calibration factor, CF, is also reported.

Table 3
Molar enthalpy of reversible adsorption, $\Delta_a h$, of propane and propene onto Cu-derivatised aluminosilicate monoliths determined in flow microcalorimetry experiment

Sample	$\Delta_a h_R$ (kJ mol^{-1})	
	Propane	Propene
SiAl20Cu7$_{EX}$	−30.9	–
SiAl20Cu2$_{IM}$	−31.9	−42.0
SiAl20Cu5$_{IM}$	−29.6	−38.3
SiAl20Cu10$_{IM}$	−25.3	−23.8
SiAl20Cu20$_{IM}$	−18.3	−25.4
SiAl20Cu2$_{DI}$	−26.2	−31.6
SiAl20Cu5$_{DI}$	−30.7	−39.1
SiAl20Cu10$_{DI}$	−36.2	−42.2
SiAl20Cu20$_{DI}$	−30.8	−42.6

Ag(I) ions dispersed over the supporting surface. Here the irreversible adsorption component is much smaller than the number of metal ion sites. On average, there is one propene molecule irreversibly adsorbed per 10 metal ions. Transition metal insertion via ion exchange from aqueous solution leads to hydrolytically induced changes in the adsorbent porosity, as shown by lower specific surface areas and greater mean pore diameters of the two adsorbents compared to the prisitine sample SiAl20 ($S_{BET} = 911\,m^2\,g^{-1}$ and $d_p = 2.4\,nm$ [8]). Comparison of surface area and porous structure parameters also suggests blockage of smaller pores. This means that only a fraction of metal ion sites are accessible to alkene molecules. When the transition metal is introduced in the synthesis stage, more or less dispersed metal oxide species are postulated to exist on the internal solid surface. It can be seen in Tables 1 and 2 that the amount of irreversible propene adsorption decreases with increasing metal content. Adding more metal in the aluminosilicate framework probably leads to the formation of bigger oxide particles on the surface of the adsorbent with the concomitant decrease in the degree of dispersion. This effect may be responsible for diminishing the irreversible contribution to propene adsorption. In the case of the impregnated materials, the irreversible adsorption component per unit surface area of the adsorbent shows an upward trend with increasing metal content, with the sole exception of SiAl20Cu5$_{IM}$ for which the surface density of irreversible adsorption is the lowest (ca. 0.17 μmol m^{-2}) amongst all samples. A preliminary XPS study shows that, in these adsorbents, Cu(II) or Ag(I) occurs mainly on the solid surface in the form of copper or silver nitrate, whereas metal oxide species constitute the second metal form. In the case of monoliths impregnated with Cu, the latter contribution attains a maximum of 20% for SiAl20Cu5$_{IM}$ and then it decreases with increasing degree of metal incorporation. The above conclusions argue against the metal oxide species as the most relevant form of Cu(II) or Ag(I) to selectively adsorb propene. For high metal loadings corresponding to 10 and 20 wt.% of metal in the sample, a significant decrease in the specific surface area is observed. Consequently, more pore blockage is expected to account for lower surface site occupancy by alkene molecules. The amount of propene irreversibly adsorbed onto samples containing 2 wt.% of copper or silver exceeds the overall metal content. This means that either several alkene molecules adsorb on one metal site or the irreversible propene adsorption can also occur on surface sites which are not directly related to the incorporated metal. Some active sites may be ascribed to the presence of extraframework aluminium. It should be noted that a maximum quantity of 6-coordinated aluminium has been obtained with monoliths containing small metal amounts [8]. Nevertheless, the addition of copper or silver is necessary for propene to be irreversibly adsorbed. The two-cycle adsorption of alkene molecules onto SiAl20 at low equilibrium pressures could not be measured because of very slow kinetics in establishing the adsorption equilibrium.

Table 4
Molar enthalpy of adsorption, $\Delta_a h$, of propane (reversible) and propene (irreversible) onto Ag-derivatised aluminosilicate monoliths determined in flow microcalorimetry experiment

Sample	$\Delta_a h_R$ (kJ mol^{-1})	
	Propane	Propene
SiAl20Ag20$_{EX}$	−33.6	−73.2
SiAl20Ag2$_{IM}$	−34.1	−98.5
SiAl20Ag5$_{IM}$	−33.1	−90.2
SiAl20Ag10$_{IM}$	−36.1	−76.9
SiAl20Ag20$_{IM}$	−32.9	−111.5
SiAl20Ag2$_{DI}$	−27.4	−90.4
SiAl20Ag5$_{DI}$	−32.3	−74.6
SiAl20Ag10$_{DI}$	−32.6	−87.2
SiAl20Ag20$_{DI}$	−35.8	−89.4

Reversible adsorption under equilibrium conditions is usually expected to have a physical character and the differential molar enthalpy of adsorption should be of the same order of magnitude as the molar enthalpy of condensation. Although the thermal effect measured in the flow experiment corresponds rather to the molar integral quantity, the enthalpy values reported in Tables 3 and 4 may be compared with the molar enthalpy of gas condensation at 298 K: −14.8 kJ mol^{-1}, propane; −14.2 kJ mol^{-1}, propene [11]. The enthalpy effect of irreversible adsorption of propene onto Ag-derivatised monoliths ranges between −73.2 and −111.5 kJ mol^{-1}, which indicates the formation of chemical bonding between the adsorbate and the solid surface. An adsorption energy of ca. −107 kJ mol^{-1} was theoretically predicted for π-complexation of propene onto Ag$^+$-exchanged resins [2]. Unexpectedly, the enthalpy effect of reversible adsorption of propane changes from −18.3 to −36.2 kJ mol^{-1} and that of propene is between −23.8 and −42.6 kJ mol^{-1}. Therefore, adsorbate–adsorbent interactions involved in the reversible adsorption of gaseous molecules on the pure solid surface under flow conditions are stronger than intermolecular forces in the liquid phase. On the one hand, weakly polar propene (dipole moment $\mu = 0.366\,D$ [11]) or propane ($\mu = 0.084\,D$ [11]) molecules of comparable polarisability (similar molar mass and boiling points) can interact more strongly with the external field created by the various metal species on the solid surface than amongst themselves in the liquid phase. On the other hand, the enthalpy enhancement may be due to weak chemisorption of hydrocarbon molecules, which are removed by the flowing carrier gas. For example, the ability of silver ions to react reversibly with alkenes forming silver–alkene complexes was observed in the separation process based on polymer membranes [12]. The coordinated alkene molecules weakly bound to silver ions in the membranes were labile enough to be readily released from active sites.

The Ag-derivatised aluminosilicates can selectively adsorb propene over propane, since the molar adsorption enthalpy of propene is twice or three times that of propane. The impregnated monoliths are characterised by higher enthalpy differences than their homologues modified by direct incorporation or ion exchange. For the same amount of metal added, the order of decreasing selectivity is $\mathrm{SiAl20Ag20_{IM}} > \mathrm{SiAl20Ag20_{DI}} > \mathrm{SiAl20Ag20_{EX}}$. No clear trends with changing metal content was observed, the first and the last samples within each series being the most selective on the basis of enthalpy considerations. Metal site characteristics such as their nature, dispersion and accessibility certainly contribute to the heterogeneity of the thermal effect. Pore blockage by growing metal clusters may diminish the number of active sites available for irreversible adsorption. Compared to the batch experiment, the effective accessibility of these sites under flow conditions is less pronounced because of a relatively short time of contact between the adsorbent and the adsorbate. When the active sites become saturated by the strongly adsorbing alkene molecules, further adsorption will certainly be reversible and characterised by much lower heat effects. Therefore, optimum metal loadings are necessary for adsorbents to selectively adsorb much propene.

The Cu-containing samples appear unselective under flow conditions, because the difference in $\Delta_a h_R$ between both gases is very small. This result is at variance with the conclusions drawn from the previous equilibrium studies. It may be that irreversible adsorption of propene on strongly active sites on the solid surface is a diffusion-limited phenomenon in the case of copper. Since the state of the molecules adsorbed under flow conditions is far from the adsorption equilibrium, only weak reversible adsorption would occur. Note that the reaction between silver sites and alkene molecules flowing through the derivatised membranes was found to be very rapid [12]. The formation of π-complexation bonds, in which the σ donation of electrons from alkene to the LUMO (lowest unoccupied molecular orbital) of the metal cation is followed by the d–π^* back-donation and electron redistribution amongst the metal d orbitals [2–5], may be more complicated, and possible less stable, in the case of Cu(II) ions having an incomplete d shell configuration. Another hypothesis is related to the initial state of the solid surface in each type of experiment. Prior to batch adsorption measurements, the surface of the adsorbent is completely purified during sample outgassing at high temperature. The thermal treatment at room temperature applied in the flow microcalorimetry experiment may be insufficient for some gases or vapours to be removed from the surface metal species. Cu(II) ions with smaller atomic number and ionic size than those of Ag(I) ions exhibit greater enthalpy of hydration. Therefore, they should be more sensitive to the poisoning effect of water vapour and the irreversible adsorption of propene is hindered onto such solids.

5. Conclusion

The results obtained in the present study clearly show that adsorption selectivity of aluminosilicate monoliths derivatised with Cu(II) and Ag(I) by ion exchange, incipient wetness impregnation or direct metal incorporation during the synthesis depends on the experimental conditions used. Under conditions allowing adsorption equilibrium to be attained, ionic metal species of both types are more appropriate than metal oxide clusters for selective adsorption of propene over propane. When the adsorption experiment is carried out under flow conditions, only Ag-derivatised samples appear selective at low surface coverages, giving a strong irreversible contribution to the molar enthalpy of adsorption. The enthalpy values for propene and propane are similar for all Cu-containing materials, irrespective of the overall metal content. The nature of the bonding between the surface and the adsorbate is not yet clear and is the subject of further study.

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