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Ethylene epoxidation on Ag catalysts supported on non-porous, microporous and mesoporous silicates

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Abstract

The ethylene epoxidation activity of Ag catalysts supported on non-porous SiO_2, microporous silicalite zeolite and mesoporous MCM-41 and HMS silicates was investigated in the present study in comparison to conventional low surface area α-Al_2O_3 based catalysts. The MCM-41 and HMS based catalysts exhibited similar ethylene conversion activity and ethylene oxide (EO) selectivity with the SiO_2 and α-Al_2O_3 based catalysts at relatively lower temperatures (up to ~230 °C), whereas their activity and selectivity decreased significantly at higher temperatures ($\geq$300 °C). The silicalite based catalyst was highly active for a wide temperature range, similar to the SiO_2 and α-Al_2O_3 based catalysts, but it was the less selective amongst all catalysts tested. High loadings of Ag particles (up to ca. 40 wt.%) with medium crystallites size (~20–55 nm) could be achieved on the mesoporous materials resulting in very active epoxidation catalysts. The HMS-type silicate with the 3D network of wormhole-like framework mesopores (with average diameter of ~3.5 nm), in combination with a high-textural (interparticle) porosity, appeared to be the most promising mesoporous support.

Keywords: Ethylene epoxidation; Silver catalysts; Mesoporous; MCM-41; HMS; Silicalite zeolite

1. Introduction

The selective oxidation of ethylene to ethylene oxide (EO) is probably one of the most important catalytic processes for the production of high added-value petrochemicals. The epoxidation reaction under industrial conditions is usually carried out at elevated pressure over silver catalysts supported on low surface area α-Al_2O_3 (SSA: 0.1–1 m^2/g). High ethylene oxide selectivity (up to 80%) can be achieved by introducing alkali (such as Cs) and halide (such as vinyl chloride) promoters to the pure supported silver catalysts, which otherwise give selectivity of 30–50%. Ethylene epoxidation on supported silver catalysts has been widely studied in previous works [1–3]. The generalized reaction mechanism is based on a triangular network in which ethylene can either convert to ethylene oxide and subsequently to CO_2 or via a parallel-path can be directly oxidized to CO_2.

Except α-Al_2O_3 several other oxides have been tested as supports of silver catalysts. Lee et al. [4] examined a series of low or relatively higher surface area oxides (α-Al_2O_3, TiO_2, SiO_2, ZrO_2, MgO, Nb_2O_5, V_2O_5, Y_2O_3) and found that all supports that were active in the isomerisation/oxidation of EO led to low or zero selectivity to EO during ethylene epoxidation with the respective Ag catalysts. The activity of the supports in EO isomerisation/oxidation was found to be proportional to their surface acidity. It is generally believed that the selectivity towards EO or CO_2 is strongly affected by the acidic properties of the support. The EO precursors (intermediate species) initially formed on silver sites, isomerise to acetaldehyde on Lewis or Brönsted type acid sites of the support. Acetaldehyde is finally oxidized on silver sites producing CO_2. Yong et al. found that SiO_2 and α-Al_2O_3 were almost inactive in the conversion of EO to acetaldehyde [5] in contrast to TiO_2 and γ-Al_2O_3 which were both very active in the above reaction due to the presence of weak Brönsted acid sites (surface hydroxyl groups). Dioxane and C_4 oxygenates were also formed with the latter two supports. Bulushev et al. [6] showed that in addition to Brönsted acid sites, the Lewis acid sites on supports such as aluminas catalyze also the isomerisation of EO to acetaldehyde. Besides the formation of acetaldehyde via isomerisation of EO, glycol-like intermediate species (–OCH_2CH_2OH) were also formed on surface basic hydroxyl groups of alumina and titania

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supports, as it was shown by infrared spectroscopy studies [5,6]. These glycol species can further be oxidized on silver sites.

Apart from the effect of acidity of catalysts supports on EO selectivity, a great deal of attention has been paid on the type of oxygen species bonded on silver atoms and how these affect the epoxidation activity. Three types of oxygen species have been proposed, the molecular, the atomic and the sub-surface oxygen [7,8], with the sub-surface oxygen promoting the epoxidation activity by inducing a more electrophilic character to the atomic oxygen bonded to silver. More recent studies suggested the initial formation of a surface oxametallacycle intermediate on silver that can either produce ethylene oxide or transform directly to acetaldehyde followed by total oxidation towards CO_2 [9].

The size of silver particles/crystals is also another important parameter that affects both activity of ethylene conversion and EO selectivity. Lee et al. [10] found that the epoxidation activity of Ag/α-Al_2O_3 catalysts shows a maximum at silver crystallite size of ~40 nm; selectivity towards EO increases with silver size of up to 40 nm, while above that size it remains almost stable. These effects can be attributed to changes in the structure and morphology of the silver crystals affecting the surfaces available for catalytic reactions [11].

With regard to the effect of surface area of catalysts supports, the majority of studies have focused on low surface area oxides, with most representative being the very low surface area α-Al_2O_3 (SSA ≤ 1 m^2/g) [3,12]. Silver catalysts supported on aluminas with relatively high surface area have also been reported [13]. The type of alumina and its porosity characteristics depend greatly on the thermal pre-treatment of aluminium oxy-hydroxide precursor compounds, such as AlO(OH) (bohemite). By increasing the severity (temperature and time) of calcination, lower surface area aluminas are obtained. Aluminas with surface areas of up to 20 m^2/g exhibited appreciable selectivity to ethylene oxide (EO) [14], while catalysts based on higher surface area aluminas (>30 m^2/g) were completely inactive for EO formation [13,14]. However, it should be pointed out that the lower calcination temperature of the alumina precursors does not result only to higher surface areas but also to relatively higher concentration of acidic surface hydroxyls (Brönsted acid sites) that lead to complete oxidation of EO intermediates to CO_2, as described above.

In contrast to aluminas, silver catalysts supported on relatively high surface area silicas (SSA up to ca. 350 m^2/g) were shown to be active in EO production, reaching in some cases EO selectivities similar to those obtained with low surface area aluminas [4,5,14]. The observed high EO selectivity with catalysts based on relatively high surface area silicas (ca. 350 m^2/g) indicates that the surface area of the support is not as crucial as other parameters, such as the acidic properties, in determining the activity and selectivity in ethylene epoxidation. Towards this direction, Giordano et al. [15,16] studied silver catalysts supported on zeolite samples (Na-X and Na-A) and found that the Ag-impregnated Na$^+$-zeolites exhibited EO selectivity comparable to that of the typical oxide-based catalysts, while the Ag-exchanged samples showed zero EO selectivity due to the presence of Brönsted acid sites, which were generated during pre-treatment of the Ag-exchanged catalysts with H_2 (reduction) before reaction. In contrast to crystalline, microporous zeolitic aluminosilicates whose catalytic activity is strongly affected by mass diffusion limitations as well as by their acidic properties, the mesoporous silicates of the MCM-type, first reported by Mobil researchers [17], can be an alternative choice for metal-supported catalysts. MCM-type materials, as well as other more recently developed mesoporous silicates (such as HMS, SBA-15, MCF), exhibit very high surface area (SSA ~700–1300 m^2/g) with tunable pore size in the range of 2–20 nm (pore diameter) and different pore structures, i.e. hexagonal (MCM-41, SBA-15), wormhole-like (HMS), and foam-like (MCF). The very high surface area and the narrow pore size distributions of the mesoporous silicates allow homogeneous dispersion of metal active sites even at high metal loadings. They possess surface hydroxyls (terminal) which are not acidic (compared to relatively strong zeolitic acidity or the acidity found in γ-Al_2O_3) and they do not induce negative effects on catalytic reaction rates due to diffusion limitations, at least for molecules as small as ethylene and ethylene oxide, or other possible intermediates in ethylene epoxidation.

For the above reasons and since there is no related work previously reported in the literature, in the present study we investigate the activity and selectivity of silver catalysts based on different mesoporous silicates in the reaction of ethylene epoxidation in comparison to catalysts based on non-porous silica, microporous silicalite and classical very low surface area α-Al_2O_3.

2. Experimental

2.1. Synthesis of mesoporous silicate supports—preparation of Ag catalysts

The silica or silicate-based materials that were used as catalytic supports were (a) a commercial non-porous silica (Sigma, SiO_2 99%); (b) a commercial microporous zeolite silicalite (UOP); (c) mesoporous siliceous MCM-41, as well as an Al-MCM-41 aluminosilicate, synthesized in the laboratory; and (d) mesoporous siliceous HMS with low- and high-textural porosity, also synthesized in the laboratory. As reference catalyst support, a very low surface area α-Al_2O_3 calcined at 1350 °C was also tested for comparison.

Siliceous MCM-41 was synthesized according to previously reported methods [18]. In a typical synthesis, 4.15 g of cetyltrimethylammonium bromide (CTAB) were dissolved in 180 g of water (double distilled water was used in all experiments) and 14.2 g of aqueous ammonia solution (25% w/w) were then added to the CTAB solution for raising the pH to ~11.5–12. In this solution, 15 g of tetraethylorthosilicate (TEOS) were added slowly under moderate stirring; the pH after TEOS addition decreased to ~10.5. The molar composition of the synthesis gel was 1TEOS:0.158CTAB:2.9NH_3:155H_2O. The resulting suspension was further stirred for 1 h and was then hydrothermally aged in closed polypropylene (PP) bottles for 5 days at 100 °C. The produced solids were filtered, washed thoroughly with 2 l water and dried overnight at 90 °C.

Al-MCM-41 was synthesized following the method described above, except that Al was added in the synthesis gel (Si/Al = 100) using aluminun isopropoxide ($Al(OiPr)_3$) as the Al source; the molar composition of the gel was $1TEOS{:}0.01Al(OiPr)_3{:}0.158CTAB{:}2.9NH_3{:}155H_2O$.

HMS-type mesoporous silicate materials with wormhole-like pore structure were synthesized based on previously reported methods [19–21]. The porosity and textural properties of HMS can be modified by changing the ratio between water and ethanol, used as solvents of the neutral amine surfactants [20,21]. A sample with low-textural porosity (HMS-1) was synthesized by dissolving 4.86 g of dodecylamine (DDA, used as structure directing agent) in 52 ml ethanol followed by addition of equal volume of water (water/ethanol = 50:50, v/v). 20.0 g TEOS were then added slowly and the mixture was stirred for 18 h at room temperature, filtered, washed with water and dried at room temperature for 24 h and at 90 °C for 3 h. The molar composition of the synthesis gel was $1TEOS{:}0.27DDA{:}9.09EtOH{:}30H_2O$. A sample with high-textural porosity (HMS-2) was prepared in a similar way as HMS-1 but with water/ethanol ratio of 90:10 (v/v) in the synthesis mixture. The molar composition of the gel was $1TEOS{:}0.25DDA{:}4.38EtOH{:}127.5H_2O$. A third sample (HMS-3) was synthesized as HMS-2 with the same gel composition, except that the aging process was carried out at 65 °C (instead of room temperature) in closed PP bottles for 18 h, in order to increase the size of the mesopores.

Ag catalysts were prepared by typical dry or wet impregnation methods using $AgNO_3$ aqueous solutions. After impregnation the catalysts were dried at 80 °C under vacuum for 3 h.

2.2. Physicochemical characterization of supports and catalysts

Chemical analysis of the samples was performed by ICP-AES using a Plasma 400 (Perkin Elmer) spectrometer, equipped with Cetac6000AT + ultrasonic nebulizer. X-ray powder diffraction (XRD) patterns were obtained using a Siemens D-500 automated diffractometer (Cu Kα radiation, $\lambda = 1.5418$ Å), in the 2θ range of 2–10° (for identification of the mesostructures) or 5–85° (for identification of Ag crystalline phases) and at a scanning rate of $1^\circ\ min^{-1}$. Scherrer analysis of XRD data was performed for the Ag-containing samples in order to determine the size of Ag crystallites. Specific surface area (SSA) and porosity characteristics of the samples were determined from N_2 adsorption/desorption isotherms, which were obtained at −196 °C on an Automatic Volumetric Sorption Analyzer (Autosorb-1, Quantachrome). Prior to the determination of the adsorption isotherms, the samples were evacuated overnight at 150 °C under 1.0×10^{-3} mbar vacuum. TEM and HRTEM images were obtained on a JEOL JEM 2010 micrometer with a LaB_6 filament and an accelerating voltage of 200 kV. The TEM specimens were prepared by evaporating one drop of a powdered sample-EtOH suspension (after sonication) onto a carbon-coated holey film supported on a 3 mm diameter, 300 mesh copper grid. The total number of acid sites of all the catalysts supports tested was measured by Temperature Programmed Desorption (TPD) of NH_3 (details are given elsewhere [22]).

2.3. Catalytic tests—epoxidation of ethylene

The catalytic tests were carried out in a bench-scale fixed bed continuous flow reactor with internal diameter of 1.1 cm. The catalysts samples were prepared by mixing 0.4 g of Ag catalyst with equal amount of quartz beads (catalyst bed height ∼1 cm, particle size 45–150 μm). Before catalytic tests, the catalysts were reduced in situ with H_2 flow at 350 °C for 2 h. The reactant feed consisted of 2% C_2H_4, 6% O_2 diluted in He (total pressure 1 bar) with total flow rate of $200\ cm^3\ min^{-1}$. The contact time, W/F, defined as the ratio of catalyst weight to total flow rate was $0.12\ g\ s/cm^3$. Actual reaction temperature was monitored by a thermocouple inserted in the middle of catalyst bed. Reactants and products streams were analysed online by gas-chromatograph (Shimadzu GC-14B) equipped with thermal conductivity detector (TCD) and porapak Q column (1/8 in., 10 ft).

3. Results and discussion

3.1. Physicochemical characteristics of silicate-based non-porous, microporous and mesoporous supports and respective Ag catalysts

The microporous zeolite silicalite and the mesoporous MCM-41 and HMS silicates were used in this study as the high surface area silicate supports for Ag catalysts. The nitrogen adsorption–desorption isotherms of all the supports tested are shown in Fig. 1. The porosity characteristics of the supports and

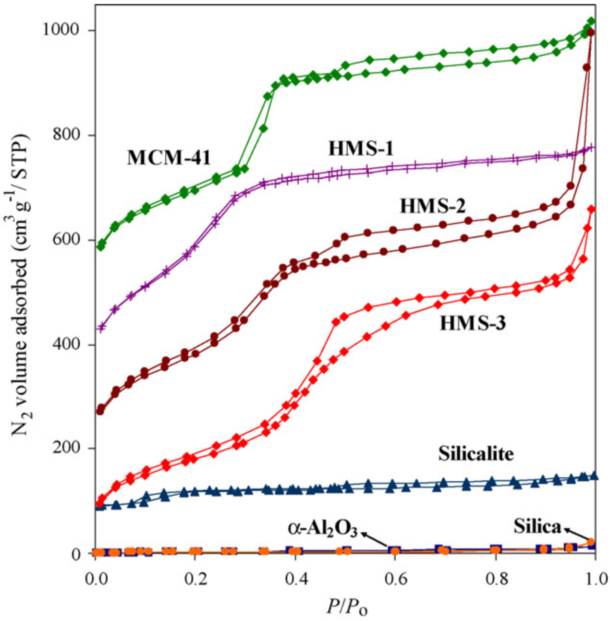

Fig. 1. Nitrogen adsorption–desorption isotherms of the non-porous (α-Al_2O_3, SiO_2), microporous (silicalite) and mesoporous (MCM-41, HMS) catalyst supports. Isotherms of HMS-2, HMS-1 and MCM-41 are offset by 150 each.

Table 1
Porous characteristics of the supports and the respective Ag catalysts—Ag crystallite sizes of the various catalysts

Support/catalyst	Surface area[a] (m^2/g)	Pore diameter[c] (nm)	Total pore volume[d] ($cm^3\ g^{-1}$)	Ag crystallite size[f] (nm)
MCM-41	895	2.87	0.88	–
Al-MCM-41	839	2.70	0.85	–
9% Ag/MCM-41	709 (773)[b]	2.87	0.72	8.2
17% Ag/MCM-41	457 (535)	2.51	0.47	9.1
23% Ag/MCM-41	211 (260)	2.71	0.27	12
41% Ag/MCM-41	415 (585)	2.70	0.44	20
HMS-1	967	2.36	0.74	–
HMS-2	867	2.79	1.31	–
HMS-3	657	3.36	1.02	–
9% Ag/HMS-1	578 (630)	2.35	0.50	11
9% Ag/HMS-2	651 (710)	2.70	0.92	7.0
9% Ag/HMS-3	583 (635)	3.36	0.94	12
41% Ag/HMS-1	–	–	–	55
Silicalite	381	~0.55[e]	0.23	–
9% Ag/silicalite	324 (353)	–	0.22	65
SiO_2 (silica)	6.6	–	0.03	–
2.4% Ag/SiO_2	≤6	–	0.02	48
9% Ag/SiO_2	≤6	–	0.02	54
17% Ag/SiO_2	–	–	–	62
41% Ag/SiO_2	–	–	–	120
α-Al_2O_3	2.1	–	0.02	–
2.4% Ag/α-Al_2O_3	≤2	–	0.01	49
9% Ag/α-Al_2O_3	≤2	–	0.01	62
23% Ag/α-Al_2O_3	–	–	–	70
41% Ag/α-Al_2O_3	–	–	–	87

[a] Multi-point BET surface area.
[b] Values in parentheses refer to normalized surface areas based on silicate weight.
[c] Determined by BJH method from nitrogen adsorption data.
[d] At $P/P_0 = 0.99$.
[e] Value taken from literature corresponding to the pore size of ZSM-5 and silicalite microporous materials.
[f] Determined by Scherrer analysis of XRD data.

representative Ag catalysts are given in Table 1. Silicalite is the siliceous analogue of ZSM-5 pentasil zeolite with a 3D pore system consisting of intersecting channels with pore aperture diameter of ~0.55 nm. The silicalite sample tested in this work has a surface area of 380 m^2/g (Table 1) and its microporous nature is depicted in the respective nitrogen isotherms shown in Fig. 1. The MCM-41 and HMS mesoporous silicates exhibit typical hexagonal and wormhole-like pore structures respectively, as has been verified by XRD and TEM measurements (not shown), and have significantly higher surface areas (~900 m^2/g) and larger pore diameters (~2.4–3.4 nm), compared to silicalite. The nitrogen isotherms of MCM-41 are typical of this type of mesoporous materials with narrow pore size distribution and average pore diameter of ~3 nm. The isotherms of the HMS mesoporous silicates are similar to those of MCM-41, except of the broader N_2 uptake step at P/P_0 values between 0.2 and 0.5 as a result of the more disordered structure of the wormhole-like type of mesopores. Another difference between MCM-41 and HMS samples is the presence of textural (interparticle) porosity in two of the HMS samples which is attributed to large mesopores generated within aggregates of very small primary particles. Detailed characterization data of the textural properties of HMS-type materials based on TEM and nitrogen sorption studies are provided in Refs. [20,21]. The HMS-1 sample is a low-textural porosity sample as it can be seen in Fig. 1, since the N_2 uptake does not increase at P/P_0 higher than ca. 0.9. On the other hand, HMS-2 is a high-textural porosity sample, as it is revealed by its nitrogen isotherms. The differences in morphology and textural characteristics between the low- and high-textural porosity samples (HMS-1 and HMS-2), which however possess framework mesopores of similar size ~2.4–2.8 nm, are expected to affect the mass diffusion properties and eventually the catalytic properties of these materials. In order to investigate the effect of framework mesopores size, a third sample (HMS-3) was synthesized by appropriate modification of the synthesis method (see Section 2) and tested also as catalyst support; HMS-3 shows also high-textural porosity as HMS-2 but possesses slightly larger mesopores with diameter of ~3.4 nm (Table 1). As far as the non-porous oxide supports (α-Al_2O_3 and SiO_2) are concerned, they exhibit very low surface area and total pore volume compared to those of the microporous and mesoporous silicates, as can be seen in Table 1.

An aluminum substituted MCM-41 sample, Al-MCM-41, with Si/Al of ~100 was also investigated as Ag catalyst support for ethylene epoxidation. The porosity characteristics of this sample are similar to those of the siliceous MCM-41 sample (Table 1). Al-MCM-41 is known to possess relatively mild acidity, compared to zeolites, of both Brönsted (due to bridging hydroxyls in the aluminosilicate framework) and Lewis type (due to extra-framework octahedral Al-(hydro)oxide species) [23]. The total number of acid sites of Al-MCM-41 is 0.04 mmol NH_3/g (measured by TPD-NH_3) compared to the negligible amount of acid sites (adsorbed ammonia) of all the siliceous microporous and mesoporous materials (MCM-41, HMS, silicalite) and the non-porous oxides (α-Al_2O_3, SiO_2) tested as catalyst supports.

The Ag catalysts supported on microporous and mesoporous silicates were prepared by typical dry impregnation method, which can result in a more controlled distribution of metal ions within the pores of the silicates compared to the wet impregnation method. However, the type and severity of the consequent catalyst thermal treatment is also very important in determining the final physicochemical properties (oxidation state, size and distribution) and catalytic function of the metal active sites. In the case of the non-porous and low surface area supports (such as SiO_2 and α-Al_2O_3), irrespective of the impregnation method, the dispersion of metal sites is usually more random and larger aggregates are formed especially at higher metal loadings. A rough estimation of the Ag crystallites size after activation of the catalysts at 350 °C under H_2 flow for 2 h was performed by Scherrer analysis of the XRD data for characteristic peaks related to metallic Ag crystalline phases. Although the experimental error of this method can be relatively high, the estimated values can provide a clear evidence of changes of the Ag metal crystallites size that depend on Ag loading or on the type of support. The XRD patterns of two representative catalysts with 9 wt.% Ag on α-Al_2O_3 and HMS-1 after pre-treatment at 350 °C under H_2 flow, are shown in Fig. 2. The characteristic peaks of Ag metallic phases can be clearly seen on both patterns; however, those for α-Al_2O_3 are more intense and sharper than those for HMS-1, revealing that larger Ag crystallites have been formed on the non-porous α-Al_2O_3 support. The data in Table 1 shows that the size of Ag crystallites on the non-porous oxide supports (SiO_2 and α-Al_2O_3) ranges from 45 to 120 nm, as the Ag loading increases from 2.4 to 41 wt.%. These values are consistent with those reported in the literature [10]. On the other hand, the Ag crystallites size on the mesoporous MCM-41 and HMS supports were significantly smaller, ranging from 7 to 55 nm for the respective Ag loadings, compared to the non-porous oxides. However, preliminary TEM studies (not shown) have revealed the formation of metallic Ag nanowires within the tubular mesopores of MCM-41 during the reductive pre-treatment step, in addition to crystallites with irregular shape on the external surface of the MCM-41 particles. The average Ag crystallite size estimated by Scherrer analysis in this case has a limited value since only a small fraction of Ag exists in the form of spherical crystallites. Based on the above, the HMS mesoporous silicates appear to be more appropriate supports for relatively high Ag loadings (>10 wt.%), leading to moderate Ag crystallite sizes, not exceeding ca. 50 nm, which are suggested to enhance ethylene epoxidation activity compared to very small or larger crystallites [10,11].

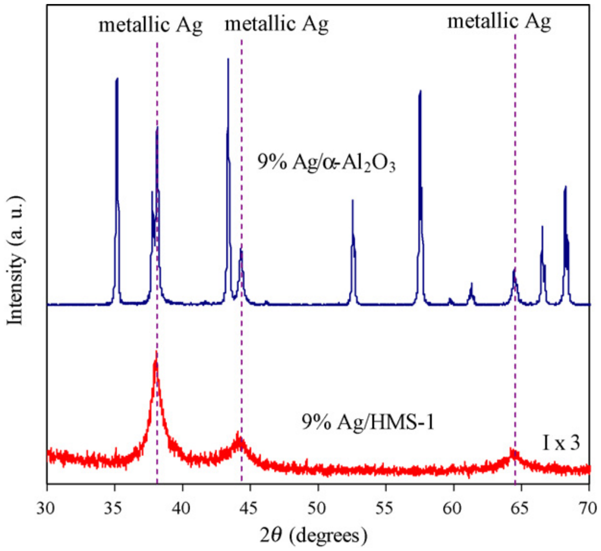

Fig. 2. XRD patterns of reduced Ag catalysts supported on α-Al_2O_3 and HMS-1 (Ag loading: 9 wt.%).

In contrast to the mesoporous supports, the size of Ag crystallites on the microporous silicalite is of much larger dimensions and is similar to those for the non-porous oxides. This was attributed to the diffusion of the Ag-impregnated ions from the interior of the micropores to the external surface of the silicalite crystals during thermal pre-treatment of the catalysts under reducing atmosphere. Consequently, most of Ag crystallites have developed relatively large sizes and reside on the surface of silicalite crystals. This has been confirmed from preliminary TEM studies (not shown) which have also verified the differences in the sizes of Ag crystallites amongst the different supports; further studies will provide evidence for the distribution and morphology of the Ag crystallites.

3.2. *Ethylene epoxidation—effect of the type of Ag catalyst support (non-porous silica, microporous silicalite, mesoporous MCM-41 and HMS)*

A list of the Ag catalysts prepared with the various non-porous and porous supports is shown in Table 1. The Ag loading of the catalysts was increased up to ca. 40 wt.% in order to identify any potential catalytic effect of the high surface area mesoporous materials that can ‘‘support’’ more silver with desirable crystallite size, compared to non-porous oxides, as described in Section 3.1. The effect of the different catalysts supports on the total ethylene conversion activity and on the selectivity towards ethylene oxide (EO) was studied with the catalysts contained 17 wt.% Ag and the results are shown in Fig. 3. The total activity for ethylene conversion (Fig. 3a) appears to be similar for all the catalysts up to a reaction temperature of ~230 °C, while above this temperature the activity of MCM-41 and HMS-1 based catalysts reaches a maximum at ~300 °C and then starts to decline. The catalyst supported on α-Al_2O_3 is the most selective one (Fig. 3b), exhibiting 40–45% selectivity to EO at conversion levels of up to 50%. The catalysts based on the two mesoporous supports (MCM-41 and HMS-1) and the non-porous SiO_2 show similar

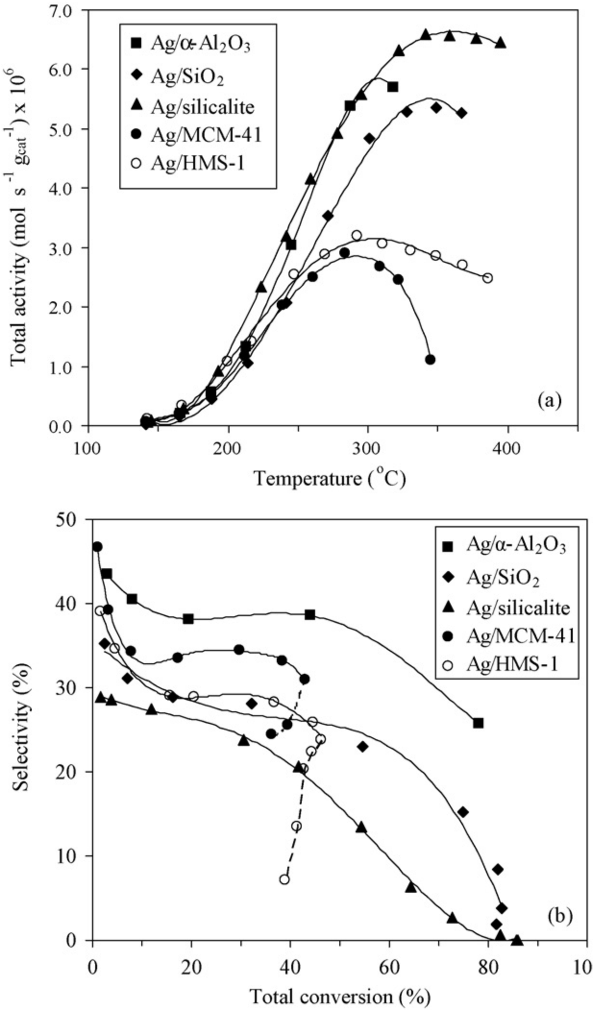

Fig. 3. (a) Total activity-rate of ethylene conversion and (b) selectivity to ethylene oxide for Ag catalysts based on non-porous SiO_2, microporous silicalite, mesoporous (MCM-41, HMS-1) silicate supports, and α-Al_2O_3 (as reference). Silver loading: 17 wt.%, $W/F = 0.12$ g s/cm^3, feed composition: 2% C_2H_4, 6% O_2, 92% He.

EO selectivity (30–40% at conversion levels of up to 50%), which is not significantly lower than that of the α-Al_2O_3 based catalysts. However, for reaction temperatures ≥300 °C, the conversion of ethylene with the MCM-41 and HMS-1 based catalysts does not increase further and their selectivity towards EO decreases sharply (Fig. 3b, dashed lines). On the other hand, the non-porous SiO_2 based catalyst shows a smoother decrease of its selectivity to EO with increasing temperature (and conversion), similar to that of the α-Al_2O_3 based catalyst. The microporous silicalite based catalyst is very active for the total conversion of ethylene, exhibiting however, lower EO selectivity compared to the rest of the catalysts, which, as in the case of SiO_2 and α-Al_2O_3, decreases smoothly with reaction temperature and conversion level (Fig. 3).

The unusual behavior of the MCM-41 and HMS-1 based catalysts could be attributed to various reasons. The most important ones relate to the partial break-down of the mesoporous structure during reaction and the subsequent trapping of silver within amorphous or crystalline silicate phases, or to the changes in the size and/or oxidation state of Ag crystallites (e.g. partial oxidation of metallic Ag to Ag$^+$ has been reported to occur more readily in relatively small Ag crystallites with size of ca. <10 nm [11,24,25]). Detailed characterization of the used catalysts based on XPS, TEM and XRD studies are in progress in order to elucidate the cause of deactivation of these Ag supported catalysts.

Although the epoxidation activity of the MCM-41 and HMS-1 based catalysts decreases significantly at reaction temperatures ≥300 °C, it should be pointed out that these temperatures are considered as relatively high for ethylene epoxidation, especially in industrial processes where the catalysts usually operate at lower ethylene conversion and higher EO selectivity. What is also more important is that the surface hydroxyls of the mesoporous silicate supports (which are not acidic as was also confirmed by the TPD-NH_3 measurements) have a limited effect on the selectivity towards EO, resulting in Ag catalysts with selectivity comparable to that of the non-porous α-Al_2O_3 and SiO_2 based catalysts. On the other hand, the catalysts supported on the Al-MCM-41 mesoporous aluminosilicate sample gave negligible EO selectivity, although its ethylene conversion activity was similar to that of the catalysts supported on siliceous MCM-41 (not shown). It is thus clear, that the low number of acid sites of Al-MCM-41 is detrimental for the epoxidation reaction, as it was expected.

3.3. Ethylene epoxidation—effect of the textural properties and pore size of HMS mesoporous supports

The HMS mesoporous silicates can be synthesized with varying framework pore size and with the presence or not of textural (interparticle) porosity, as is described in the experimental and the catalysts characterization sections, and in more detail in Refs. [20,21]. The samples with the high-textural porosity are expected to improve framework access by decreasing diffusion limitations, mainly of relatively big reactant molecules, and to enhance the transfer of products to the main gas stream, thus preventing undesirable secondary reactions on the active sites. In the present study, the sizes of reactants, products and potential intermediates species are considered to be sufficient smaller than those of both the framework mesopores (2.4–3.4 nm) and the large interparticle mesopores (>20 nm) of the HMS materials. As a consequence, the 9 wt.% Ag catalysts supported on both HMS-1 (low-textural porosity) and HMS-2 (high-textural porosity) silicates exhibited similar epoxidation activity, as can be seen in Fig. 4. However, the catalyst based on HMS-3, which apart from the high-textural porosity possesses also slightly bigger framework mesopores (diameter 3.4 nm) compared to HMS-1 and HMS-2, is significantly more active that both the HMS-1 and HMS-2 based catalysts. Interestingly, this sample is also more active than the respective α-Al_2O_3 and SiO_2 based catalysts, at least at reaction temperatures of up to ~280 °C (Fig. 4a). The selectivity to EO for all the above catalysts is similar (35–45%), at least at reaction temperatures of up to 300 °C and conversion levels of up to 40%; at higher reaction temperatures the HMS based catalysts show the previously

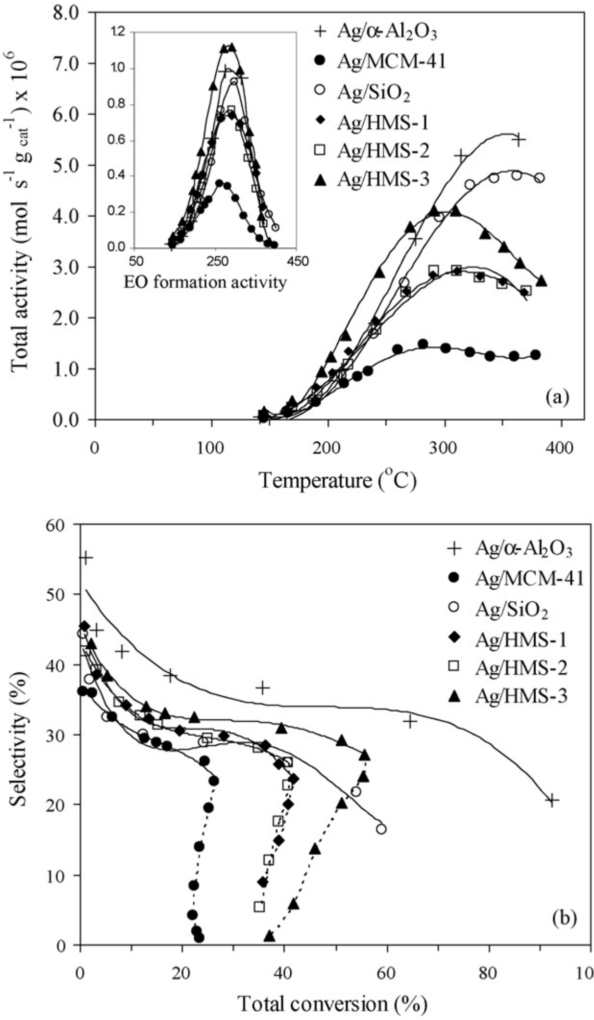

Fig. 4. (a) Total activity-rate of ethylene conversion and (b) selectivity to ethylene oxide for Ag catalysts based on mesoporous silicates with different pore sizes and structures. Non-porous SiO_2 and α-Al_2O_3 based catalysts are included for comparison. The inset shows the ethylene oxide formation rate vs. temperature for the various catalysts. Silver loading: 9 wt.%, $W/F = 0.12$ g s/cm^3, feed composition: 2% C_2H_4, 6% O_2, 92% He.

discussed unusual steep drop of their selectivity accompanied by decrease of their total conversion activity (Fig. 4b).

All the HMS based catalysts with 9 wt.% Ag were more active than the respective MCM-41 based catalyst, as it is shown in Fig. 4. This can be attributed to the formation of metallic Ag nanowires within the tubular mesopores of MCM-41, as described above, which renders a significant fraction of active Ag sites inaccessible to C_2H_4 reactant molecules since the surfaces of the Ag wires are covered by the silicate walls of the mesopores.

3.4. Stability of Ag-based catalysts

In order to evaluate the stability of the Ag catalysts, and mainly that of the MCM-41 and HMS based ones, we performed time-on-stream catalytic testes at two different temperatures, 210 and 260 °C. The ethylene conversion activity and selectivity to EO against reaction time for the catalysts with 9 wt.% Ag supported on α-Al_2O_3, SiO_2, MCM-41 and HMS-3, are shown in Fig. 5. At the low reaction temperature (210 °C) the rate of ethylene conversion is stable over a period of 400 min for the α-Al_2O_3 and SiO_2 based catalysts, while the rate for the MCM-41 and HMS-3 based catalysts stabilizes after an initial period of ca. 100 min. Interestingly, the catalysts supported on mesoporous materials exhibit stable EO selectivity (30–35%) and similar to that of the α-Al_2O_3 and SiO_2 based ones. At 260 °C, the rate of ethylene conversion for the HMS-3 based catalyst is similar to that of the α-Al_2O_3 and SiO_2 based catalysts for the first minutes of the test, and after that initial period it decreases gradually and stabilizes at much lower level. The rate for the MCM-41 based catalyst is much lower compared to those for the rest of the catalysts. As far as selectivity to EO is concerned at 260 °C, the HMS-3 based catalyst remains still quite selective and stable, at levels similar to those measured for the α-Al_2O_3 and SiO_2 based catalysts.

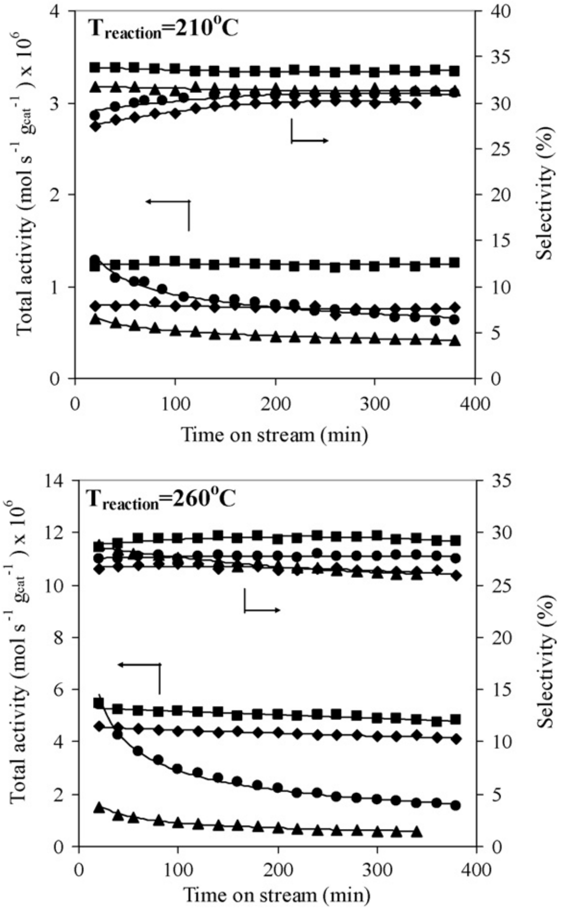

Fig. 5. Total activity-rate of ethylene conversion and selectivity to ethylene oxide vs. time-on-stream, at reaction temperatures of 210 °C and 260 °C, for Ag catalysts based on non-porous SiO_2 (◆), mesoporous silicates MCM-41 (▲) and HMS-3 (●), and α-Al_2O_3 (■) as reference. Silver loading: 9 wt.%, feed composition: 2% C_2H4, 6% O_2, 92% He.

3.5. Ethylene epoxidation—effect of Ag content of catalysts

The effect of Ag loading on total ethylene conversion and EO selectivity was tested over the α-Al_2O_3, SiO_2, MCM-41 and HMS-1 based catalysts at the reaction temperature of 220 °C

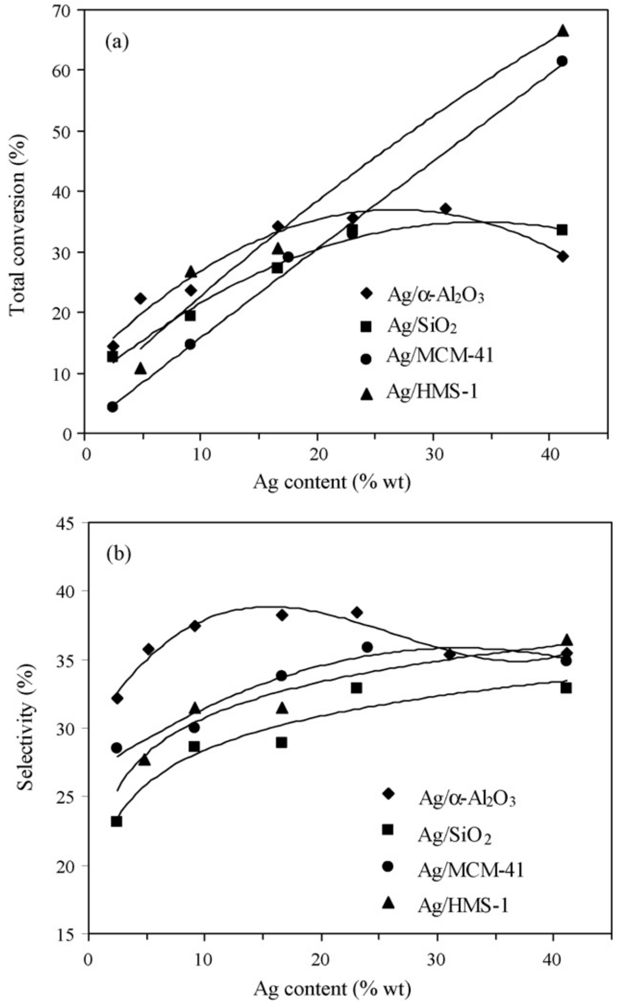

Fig. 6. (a) Ethylene conversion and (b) selectivity to ethylene oxide for catalysts with different silver loadings on various non-porous and mesoporous supports (T_{reaction}: 220 °C, *W*/*F* = 0.12 g s/cm^3, feed composition: 2% C_2H_4, 6% O_2, 92% He).

(Fig. 6). The conversion activity of the non-porous α-Al_2O_3 based catalysts increases from ~2.5 to ~20 wt.% Ag, remains stable up to about 30% and then exhibits a slight decrease, as shown for the sample with 41 wt.% Ag. The SiO_2 based catalysts exhibit similar behavior, except that the activity of the highly loaded samples remains almost stable. The EO selectivity profiles of both the α-Al_2O_3 and SiO_2 based catalysts show a similar trend with those of ethylene conversion for the respective catalysts. In contrast to the non-porous supports, the two mesoporous supports MCM-41 and HMS-1 induce a continuous increase in ethylene conversion activity with increasing Ag content, reaching ~60–65 wt.% conversion at 41 wt.% Ag loading (Fig. 6a). EO selectivity, which is at the same levels (30–35%) with those of the non-porous based catalysts, shows a similar trend but with relatively small variations with increasing Ag content (Fig. 6b). The data presented in Fig. 6 could be indicative of the correlation between the Ag crystallites size and ethylene epoxidation activity for the different catalysts/supports, since each Ag loading corresponds to a certain average crystallites size (Table 1). It is obvious that the mesoporous silicates can "support" a relatively high content (ca. 40 wt.% Ag) of medium size Ag crystallites (ca. 20–55 nm), resulting in very active epoxidation catalysts (from the data in Fig. 6, EO yield with the 41 wt.% Ag/HMS-1 or MCM-41 based catalysts is estimated to ~20%, against ~10% with the corresponding α-Al_2O_3 catalyst). Such high Ag loadings, accompanied by relatively medium size crystallites, are difficult to be achieved on non-porous supports following typical impregnation methods, thus limiting the total conversion activity of these catalysts. In order, however, to establish a relationship between Ag crystallites size on mesoporous supports and epoxidation activity, the issues of the unusual deactivation at higher reaction temperatures should be first clarified.

4. Conclusions

Ag catalysts supported on MCM-41 and HMS mesoporous silicates are active in ethylene epoxidation reaction, exhibiting ethylene oxide (EO) selectivity similar or slightly lower to that of the non-porous SiO_2 and the conventional low surface area α-Al_2O_3 based catalysts. However, this behavior has been observed only at relatively lower reaction temperatures (up to ~230 °C), while above 300 °C the epoxidation activity of both the MCM-41 and HMS based catalysts decreases at a much faster rate than with the α-Al_2O_3 and SiO_2 based catalysts. The catalysts based on microporous zeolite silicalite are very active in ethylene conversion but exhibit relatively low EO selectivity. Amongst the two types of mesoporous silicates, the HMS wormhole-like structure provides the most appropriate support for preparing catalysts with moderate Ag loadings (up to ca. 20 wt.%). The main benefit of using HMS and MCM-41 mesoporous materials is their ability to support very high loadings of Ag (ca. 40 wt.%) without increasing the size of Ag crystallites more than ca. 20 nm. As a consequence, the highly loaded mesoporous-based catalysts show very high ethylene conversion activity (up to 65%) at relatively low temperatures (~220 °C), with acceptable ethylene oxide selectivity (~30–35%). Although the Ag catalysts supported on mesoporous materials appear to be relatively stable and selective to EO at low reaction temperatures, further characterization studies of the fresh and used catalysts are required in order to draw secure conclusions regarding their performance in ethylene epoxidation reaction.

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References

[1] J.G. Serafin, A.C. Liu, S.R. Seyedmonir, J. Mol. Catal. A: Chem. 131 (1998) 157.

[2] X.E. Verykios, F.P. Stein, R.W. Coughlin, Catal. Rev.-Sci. Eng. 22 (1980) 197.

[3] R.A. Van Santen, H.P.C.E. Kuipers, Adv. Catal. 35 (1987) 265.

[4] J.K. Lee, X.E. Verykios, R. Pitchai, Appl. Catal. 44 (1988) 223.

[5] Y.S. Yong, E.M. Kennedy, N.W. Cant, Appl. Catal. 76 (1991) 31.

[6] D.A. Bulushev, E.A. Paukshtis, Y.N. Nogin, B.S. Bal'zhinimaev, Appl. Catal. A: Gen. 123 (1995) 301.

[7] D.I. Kondarides, X.E. Verykios, J. Catal. 143 (1993) 481.

[8] P.J. Hoek, E.J. Baerends, R.A. Van Santen, J. Phys. Chem. 93 (1989) 6469.

[9] S. Linic, M.A. Barteau, J. Am. Chem. Soc. 125 (2003) 4034.

[10] J.K. Lee, X.E. Verykios, R. Pitchai, Appl. Catal. 50 (1989) 171.

[11] S.N. Goncharova, E.A. Paukshtis, B.S. Bal'zhinimaev, Appl. Catal. A: Gen. 126 (1995) 67.

[12] H. Kanoh, T. Nishimura, A. Ayame, J. Catal. 57 (1979) 372.

[13] C.F. Mao, M.A. Vannice, Appl. Catal. A: Gen. 122 (1995) 61.

[14] P. Harriott, J. Catal. 21 (1971) 56.

[15] N. Giordano, J.C.J. Bart, R. Maggiore, Zeitschrift Fur Physikalische Chemie-Wiesbaden 124 (1981) 97.

[16] N. Giordano, J.C.J. Bart, R. Maggiore, Zeitschrift Fur Physikalische Chemie-Wiesbaden 127 (1981) 109.

[17] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 1083.

[18] M. Grün, K.K. Unger, A. Matsumoto, K. Tsutsumi, Micropor. Mesopor. Mater. 27 (1999) 207.

[19] P.T. Tanev, T.J. Pinnavaia, Science 267 (1995) 865.

[20] T.R. Pauly, T.J. Pinnavaia, Chem. Mater. 13 (2001) 987.

[21] T.R. Pauly, Y. Liu, T.J. Pinnavaia, S.J.L. Billinge, T.P. Rieker, J. Am. Chem. Soc. 121 (1999) 8835.

[22] K.S. Triantafyllidis, A.A. Lappas, I.A. Vasalos, Y. Liu, H. Wang, T.J. Pinnavaia, Catal. Today 112 (2006) 33.

[23] A. Corma, V. Fornes, M.T. Navarro, J. Perez-Pariente, J. Catal. 148 (1994) 569.

[24] X.E. Verykios, F.P. Stein, R.W. Coughlin, J. Catal. 66 (1980) 368.

[25] J. Lu, J.J. Bravo-Suárez, A. Takahashi, M. Haruta, S.T. Oyama, J. Catal. 232 (2005) 85.