Model silica-alumina acid catalysts for surface science and catalysis studies prepared by argon ion beam sputter deposition using HY-zeolite targets

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Thin films of silica-alumina were prepared by argon ion beam sputter deposition on gold foil using different HY-zeolites as targets. X-ray photoelectron spectroscopy (XPS) results on thin films (<10 nm) revealed that the Si/Al ratio in the films initially decreases with deposition time, but later becomes very similar to that of the target zeolite. Similarly, the position of O 1s, Al 2p, Si 2p peaks converged to the binding energies for zeolite target used. Based on the line shape of the O KVV Auger transition, we find that there is no segregation of silica and alumina in the films. By scanning electron microscopy (SEM) and scanning Auger electron spectroscopy (SAE) the thin films appear homogeneous. X-ray diffraction (XRD) results on thicker films (~ 1 μm) indicate that the silica-alumina layers are amorphous.

To test the catalytic activity cumene cracking was performed in a glass reactor. The sputter deposited thin silica-alumina films were active in cumene cracking at 573 K but at least a total of 20 cm^2 macroscopic surface area was needed to easily distinguish the activity of the film from the background activity. Similar thin films prepared from alumina or silica or the a mixture of the two were inactive. Thus, the sputtered thin film retains some chemical memory of the target.

Keywords: Zeolite thin films; sputter deposition of zeolites; ion beam deposition of zeolites; model acid catalysts

1. Introduction

Combined surface science and catalysis studies of single crystal model catalysts have made significant contributions to the understanding of catalytic processes taking place on metal surfaces [1,8]. Applied to acid catalysts, made of

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silica and alumina for example, a similar approach should be very useful. It is not easy, however, to prepare low surface area samples that are catalytically active and that are amenable to surface science investigations.

Acid catalysts are usually porous, high surface area materials. The catalytic reactions take place mostly on the internal surfaces, which are not accessible to surfaces analysis techniques, since these probe only the outmost 5 nm of the solid. There is no reason to believe that these external layers are compositionally, chemically or structurally representative samples of the entire material. For example, it has been shown by several techniques that the chemical composition of the external surface layers of zeolite particles is different from the bulk composition [2–4].

We have been trying to develop model acid catalytic systems that could be studied in ways similar to model metal catalyst. Ideally, one would like to have a thin layer of such material on a conductive substrate. A thin layer is necessary, (< 10 nm) so that the surface analytical techniques would provide information on the composition of most of the catalyst, and it should be deposited on a conductive substrate to minimize charging problems, often encountered in electron spectroscopy studies of insulators.

Recently, Davis et al. [5] synthesized zeolites on metal substrates. These films adhered very well to the metals and by stopping the crystal growth at an early stage, they could not prepare a uniform thin layer zeolite particles directly attached to the metal. The crystalline phase most likely formed on an amorphous base, thus from the surface science point of view, these mixed disordered and crystalline high surface area systems cannot offer any advantage.

It is generally accepted that the enhanced acidity of silica-alumina compared to silica and alumina is due to the presence of tetrahedral aluminum ions in Si-O-Al bridges. Thin layers of intimate mixture of silica and alumina on a conductive substrate might serve as good model acid catalysts. Ion beam sputter deposition seemed to be an attractive method to prepare such layers, because secondary ion mass spectroscopy (SIMS) and fast atom bombardment mass spectroscopy (FABMS) results had indicated [3,4] that the major species sputtered off surfaces of silica and alumina, as well as from zeolites, are atomic Si, Al and O species, and clusters like charged SiOSi, SiOAl and AlOAl are also present, but they are much less abundant. The mass distribution of the largest fraction of the sputtered species that are neutral is not known.

In this paper we report the deposition of thin homogeneous silica-alumina films on polycrystalline gold foils using zeolite targets. After deposition the samples were characterized by X-ray Photoelectron Spectroscopy (XPS), Scanning Auger Electron Microscopy (SAM), Scanning Electron Microscopy (SEM), and X-ray Diffraction (XRD). The catalytic properties were tested in cumene cracking.

The films (< 10 nm) showed significant catalytic activity that is easily distinguishable from the background if we used a surface area of at least 20 cm^2.

2. Experimental

2.1. PREPARATION OF SPUTTER DEPOSITED THIN FILMS

We used two ultra-high vacuum deposition systems. a) One to study the deposition process and the surface properties of the films, and b) a more efficient sputter deposition system, to prepare samples for the catalytic work.

a) The deposition was carried out in a sample preparation chamber connected to a commercial ESCA system (Perkin-Elmer, PHI 5300). In the preparation chamber, a 2 kV Ar^+-ion beam of about 1 cm^2 bombarded a 1.8 cm diameter Y zeolite disc at about 50–60° off from the surface normal (fig. 1). The room temperature polycrystalline gold substrate was positioned at 1–1.5 cm from the target in the direction of the surface normal. The ion gun was operated at 20 mA emission and at 1×10^{-2} Pa argon pressure. After deposition the specimen could be transferred to the XPS analyzing chamber without exposing it to the atmosphere. Utilizing a Mg source (15 kV, 300 W), survey spectra in the 0–1100 eV region and multiplex spectra for the Si 2p, Al 2p, Au 4f, O 1s, O KVV and C 1s regions were recorded.

As internal references, the C 1s and the Au 4f lines were used and fixed at 284.6 eV and at 83.8 eV, respectively. Due to the clean nature of the deposition process, adventitious carbon was always absent on the films, and only gold was used as reference: we placed a small piece of gold foil near the target so a small amount of gold was also sputtered onto the samples with the silica and alumina species. Gold was also sputter deposited on the bulk samples, and we could use both referencing techniques. Charge buildup of up to 7 volts for the bulk and up to 3 volts for the thin (< 10 nm) films were common.

b) Samples for the catalytic studies were prepared in an ion beam micro sputterer system of Varian Group, Inc. (Model 705). To obtain homogeneous films and increase the deposition rate, the geometry of the micro sputterer was slightly modified such that the gold substrate was parallel with the target and

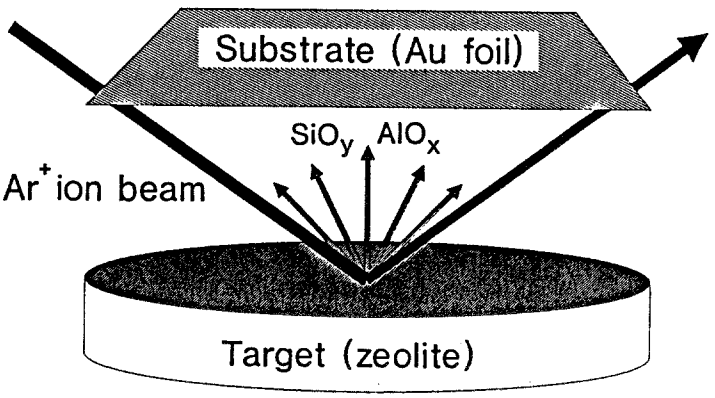

Fig. 1. Geometry for the argon ion beam sputter deposition of silica-alumina.

the distance between them was approximately one centimeter. The argon pressure was 3×10^{-2} Pa. The beam voltage and the emission current were 5 kV and 4 A, respectively.

Films were deposited on both sides of a $1 \times 1 \times 0.0025$ cm foil for 1–1 hour. To determine the deposition rate and to find out if the films show any sign of crystallinity, we carried out the deposition for 100 hours. The thickness of this film was estimated to be one micron using SEM. XRD results indicated that these films were amorphous.

In each catalytic run we used ten pieces of gold foil. Each had about 2 cm^2 total geometric surface area, and the thickness of the silica alumina layer was about 10 nm.

The target materials were HY zeolites: HY-82 (Si/Al = 1.3) and HY-62 (Si/Al = 2.1) from Union Carbide, dealuminated HY (Dow Chemical Co.), amorphous SiO_2 (Cab-O-Sil L-90, Cabot Co.) and amorphous Al_2O_3 (Aluminium Oxid C, Degussa), pressed into 1.8 cm diameter disc using a hydraulic press. The substrate was gold foil of 99.99% purity.

2.2. CATALYTIC STUDIES

To investigate the catalytic properties of the sputter deposited silica-alumina layers on gold, first we tried to use a traditional ultra-high vacuum-high pressure catalytic reactor system now routinely used in model metal catalysis studies [8].

We prepared a silica-alumina thin film on both sides of a $1 \times 1 \times 0.0025$ cm gold foil in ultra high vacuum. The deposition process was followed by Auger electron spectroscopy. After deposition the sample was introduced into the high pressure cell, and we attempted to run several typical acid catalytic reactions: 1-butene double bond shift, dehydration of iso-propanol and cumene cracking.

The activity of the 2 cm^2 sputter deposited film in any of these reactions, was only 10–20% higher than that of the gold substrate alone. All our attempts at decreasing the background activity or increasing the activity of the film by at least an order of magnitude, have failed. We have to mention here that we have been trying to detect the activity of a 2 cm^2 total surface area model catalysts in a stainless steel reactor of about 100–150 cm^2 area exposed to reactants at temperatures only somewhat lower than the reaction temperature. And it is well known that the number of active sites per unit surface area on real life silica-alumina catalysts is two to three orders of magnitude lower than on metals.

In order to detect catalytic activity we increased the macroscopic surface area of our samples to 20 cm^2 by simply using ten pieces of gold foil, 2 cm^2 each. Instead of the stainless steel high pressure reactor cell, cumene cracking was performed in an all glass system equipped with a Teflon circulation pump. The reactor loop could be pumped down to 10^{-6} Pa using a diffusion pump prior to the catalytic runs. The samples were transferred from the micro sputterer

through air and preheated in the reactor at 723 K and 2×10^{-6} Pa for 10 hours. After this pretreatment the reactor was filled to 10^5 Pa with dry nitrogen, the sample was heated to reaction temperature (570 K) and 0.002 ml liquid cumene was injected. The total volume of the system was about 200 ml. Gas samples were taken with a six port valve incorporated in the reactor loop, and introduced into the gas chromatograph (Hewlett-Packard, 5790A, 0.1% SP1000 on 80/100 Carbopack C).

Cumene from Aldrich was used containing ethyl and n-propyl benzene as contaminants (0.3 and 0.1%, respectively) determined by GC-MS analysis.

3. Results and discussion

3.1. CHARACTERIZATION OF SPUTTER DEPOSITED SILICA-ALUMINA THIN FILMS

The deposition process was followed by XPS. The prepared films were very clean and since targets where decationized only Au, Si, Al, and O peaks were present in the spectra.

In figs. 2a and 2b, we plot the integrated XPS areas for the Au 4f, O 1s, Si 2p and Al 2p peaks as function of sputter deposition time in the experiment when Y-62 was the target. (Very similar trends in the uptake curves were observed for the Y-82 and the dealuminated zeolite Y targets.) The curves can be described by simple exponential functions characteristic of three dimensional film growth. This growth mode requires that the surface species have no mobility [6]. According to SIMS and FABMS results by Dwyer et al. [3,4], the majority of fragments leaving zeolite samples are atomic Si, Al and O species, and some dimers. It is expected that these, after landing on the surface do not have appreciable mobility at room temperature and they stay where arrived and form three dimensional islands. This also implies that the developing film is most likely amorphous.

The atomic concentrations in the topmost atomic layers can be calculated based on the sensitivity factors provided with the ESCA system by Perkin Elmer ($S_{Si}/S_{Al} = 1.48$). Figs. 3a and 3b show that while the O/Si atomic ratio is constant during the entire course of deposition, the Si/Al ratio initially changes rather dramatically. First the Si/Al ratio is higher than in the target then it approaches the same value as in the target.

This can be due to one or more of the following three factors: 1) – higher silica concentration on the surface of the target, 2) – preferential sputtering of $Si(-O_y)$ species, and 3) – lower sticking probability of the $Al(-O_x)$ species.

In fig. 3b we indicated the surface composition of the target zeolite as well as its calculated bulk composition. In agreement with Barr and Lishka [2], we found that the surface of the zeolite samples was richer in silica. On the other hand Suib et al. [2c] reported that surface and bulk compositions were identical.

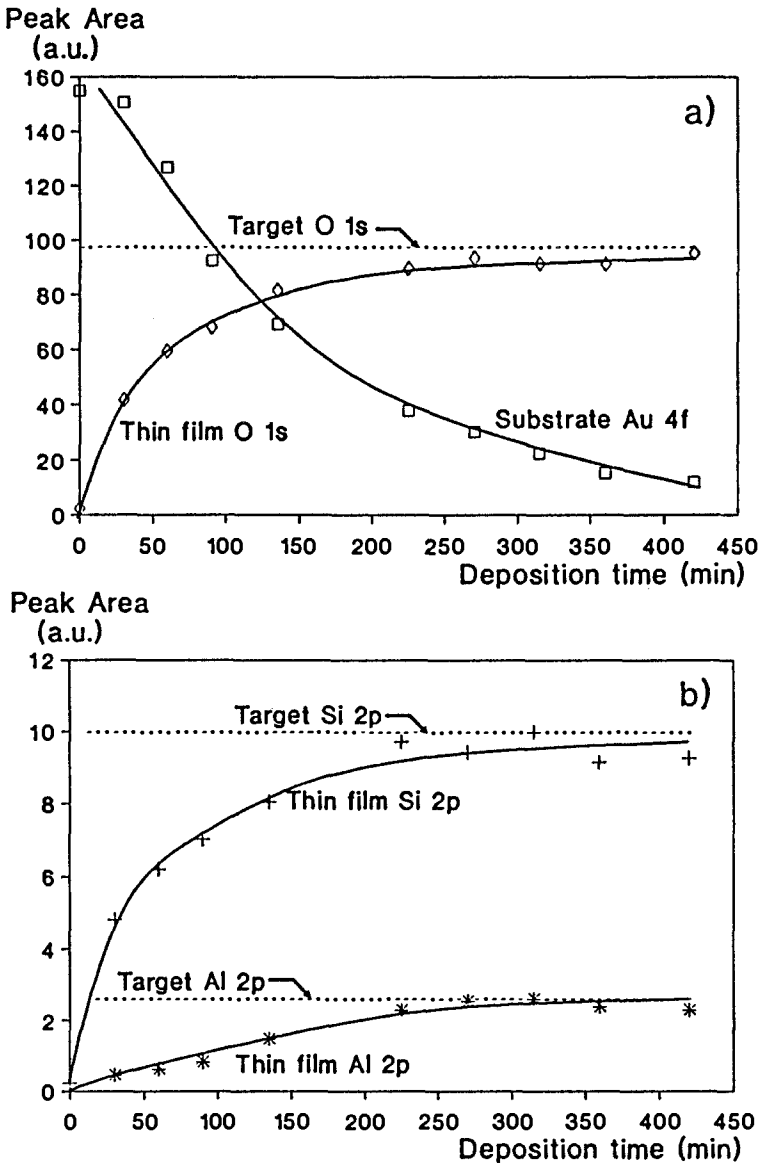

Fig. 2. Ion beam sputter deposition of silica-alumina on gold foil using Y zeolite (Y-62) as target. Integrated XPS peak intensities as a function of deposition time: a) O 1s and A 4f peak areas; and b) Si 2p and Al 2p peak areas.

They pointed out that the history and the preparation of the sample is probably more important than the type of zeolite under investigation. Quantitatively, however, a higher Si/Al ratio on the target surface alone cannot explain why we have a higher silica concentration in our sputter deposited film initially: The Si/Al ratio in the films is 3–4 times higher than the ratio determined for the surface of the zeolite sample.

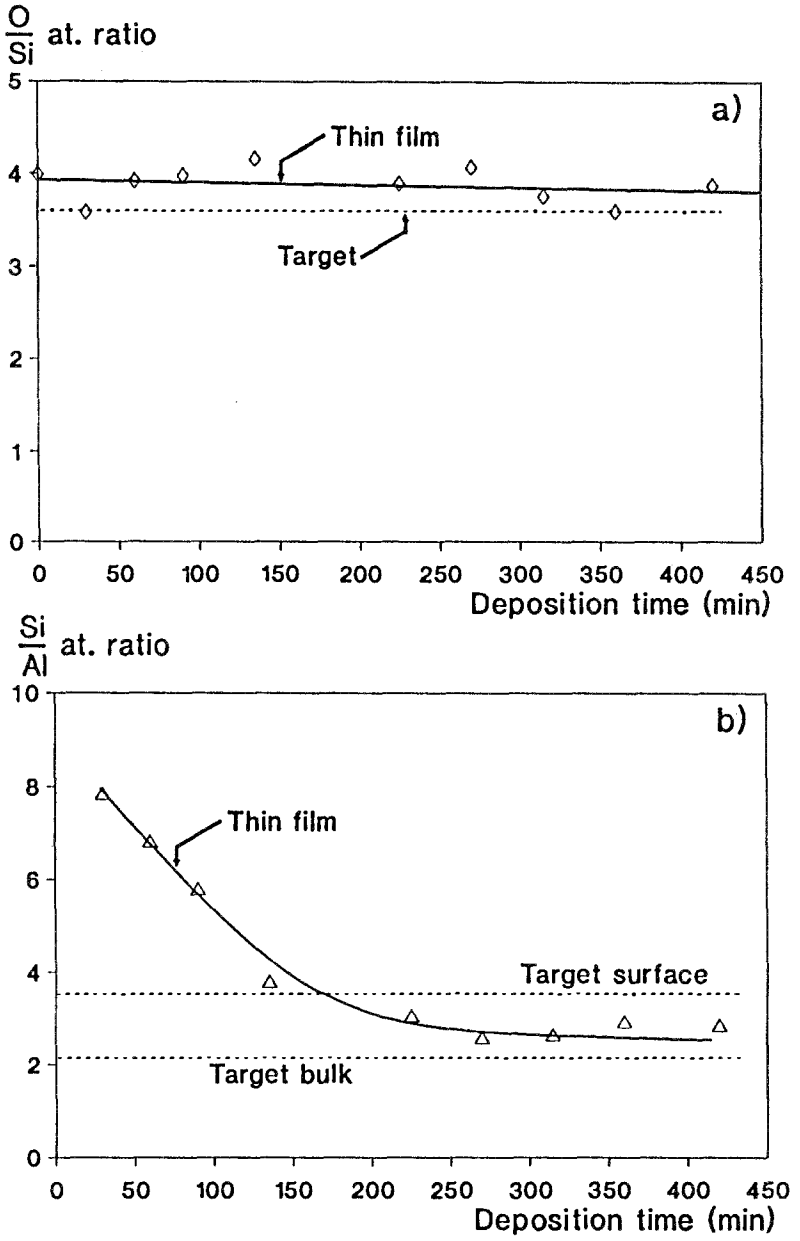

Fig. 3. Ion beam sputter deposition of silica-alumina on gold foil using Y zeolite (Y-62). Atomic concentration ratios as a function of deposition time: a) O/Si atomic ratio; and b) Si/Al atomic ratio. Horizontal lines indicate values obtained for the target.

Ar^+ ion sputtering is a common surface science method to clean surfaces. When more than one component is present on the surface, one or the other element is more readily sputters. In the literature, extensive experimental and

theoretical efforts have been made to understand the phenomenon of preferential sputtering [7]. In general, similar atomic weight species sputter with similar rate unless they have different chemical bonding on the surface [7b]. In our case silicon and aluminum are neighbors in the periodic table and it is not expected that based on the atomic weight one would sputter faster than the other. From this point of view it would be interesting to investigate the role of the zeolitic structure of the target material in preferential sputtering of the $Al(-O_x)$ and $Si(-O_y)$ species.

It is interesting that, although Ni and Cu are also next to each other in the periodic table and have very similar atomic weights, Ni sputters preferentially from a 50% Ni–50% Cu alloy. Shimizu et al. [12] found that the composition of the sputter deposited Ni–Cu films, using this alloy as target, initially changes with the target composition, but after prolonged sputtering (deposition) the composition of the film was identical to that of the bulk alloy. Because of conservation of mass, this should be true for any material after sufficiently long sputtering. The film composition has to be equal to the bulk composition unless the target is non isotropic or some species sputter in certain directions more readily.

Finally, we cannot rule out the possibility that the sticking probability of the $Al(O_x)$ and/or $Si(O_y)$ species changes with the composition of the film. This would mean that either the sticking probability of the $Al(O_x)$ species is smaller on or the sticking probability of $Si(O_y)$ species is higher on silica rich films. We cannot rule out this possibility because the Si/Al ratio is always higher initially if one starts with a clean gold substrate no matter how many times the target had been used. Thus, the changing ratio has to be the property of the substrate and/or that of the film. Neither preferential sputtering nor initially rich silica surface could explain this.

Fig. 4 shows the binding energies of Si 2p, Al 2p and O 1s electrons as a function of deposition time. The Si 2p and O 1s binding energies behave similarly. Initially they are lower than the ones for the bulk material but with increasing deposition time they become closer and closer to the bulk values. As we saw in fig. 3a, the oxygen to silicon ratio is unchanged during the entire deposition. Thus the deviation from the bulk binding energy of the O 1s and Si 2p is associated with the absence of alumina. The binding energy of the Al 2p follows a slightly different pattern. It increases with increasing film thickness, but it does not approach the value obtained for bulk HY-62. All binding energies reported here are well within the range of binding energies published for Y zeolites [2,10].

An interesting feature of the oxygen Auger line in the XPS spectra is that it can provide some structural information. Wagner et al. [10], based on slight differences in the line shape, classified the O KVV transitions in Al-Si-O compounds into three groups: I. aluminum oxides and hydroxides, and silicates, II. uncharged silica networks having Si-O-Si bonds only, and III. compounds

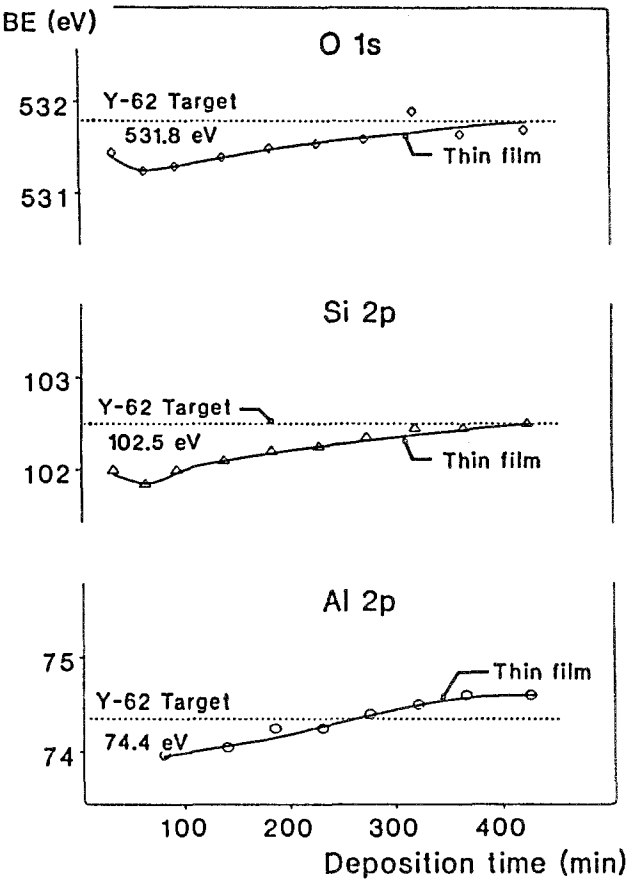

Fig. 4. Binding energies of the O 1s, Si 2p and Al 2p electrons in the sputter deposited silica-alumina film as a function of deposition time.

with high concentration of tetrahedral aluminum ions in molecular sieves. We wanted to see if this classification can be used to extract structural information from the spectra.

A few typical O KVV Auger lines obtained in this work are shown in figs. 5 and 6. Spectrum a) in fig. 5. from a dealuminated Y zeolite which belongs to group II. of the above classification shows a well defined shoulder on the lower electron kinetic energy side of the peak maximum, as expected. This feature is also present in the spectrum obtained from the sputter deposited film (fig. 5b).

In fig. 6a we show the O KVV line for the Y-82 target (Si/Al = 1.3). The line is rather sharp and no shoulder at lower electron kinetic energy is visible, only one at higher electron kinetic energy side of the maximum. This line shape does not fit in any category of the classification developed by Wagner [10]. Fig. 6b shows the oxygen Auger peak from the same Y-82 sample after thermal decomposition at 1470 K for 10 hours in helium. As confirmed by XRD this treatment eliminated the Y zeolite structure, and produced a mixture of

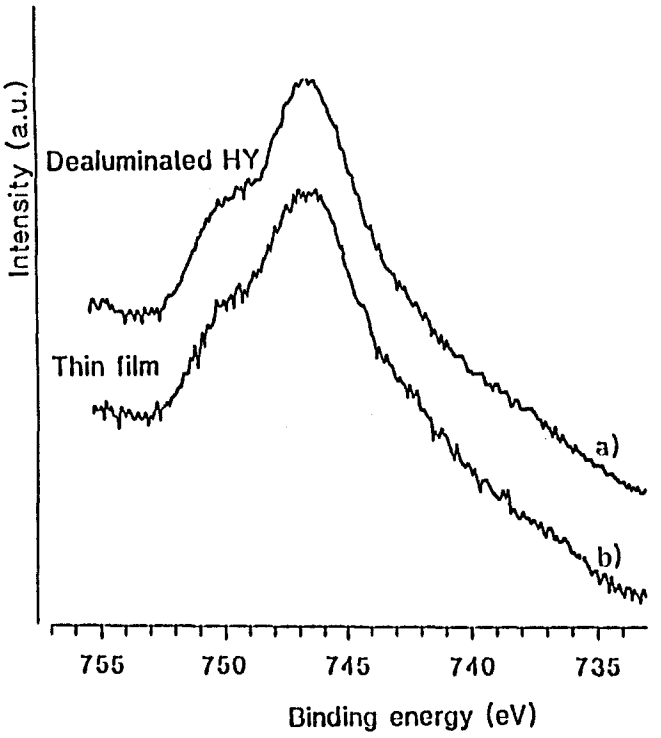

Fig. 5. Oxygen O KVV Auger transitions: a) dealuminated Y zeolite target; b) sputter deposited thin film using dealuminated Y zeolite. (Electron kinetic energy = 1253.6 eV – binding energy.)

amorphous silica and alumina. As a result, the shoulder characteristic of uncharged Si-O-Si units appears on the oxygen Auger line (fig. 6). It is interesting that this shoulder is absent if the target has been aluminum containing zeolite Y or a mechanical mixture of silica and alumina. Note, that the other shoulder at about 740 eV electron binding energy (Mg X-ray source) is still present after the loss of crystallinity. Although these differences appear minor they can be used as structural fingerprints. Especially in the future if line shapes for more Si-O-Al compounds become available.

From the XPS results we conclude that the films deposited by argon ion beam sputtering are homogeneous mixtures of silica and alumina having a very similar composition to the Y zeolite used as target. XPS results revealed that the silicon, aluminum and oxygen environments are also very similar to those of the target.

3.2. CATALYTIC STUDIES

The silica-alumina films were prepared using both the zeolite Y-82 and a mechanical mixture of silica and alumina as targets. Also, we prepared separate

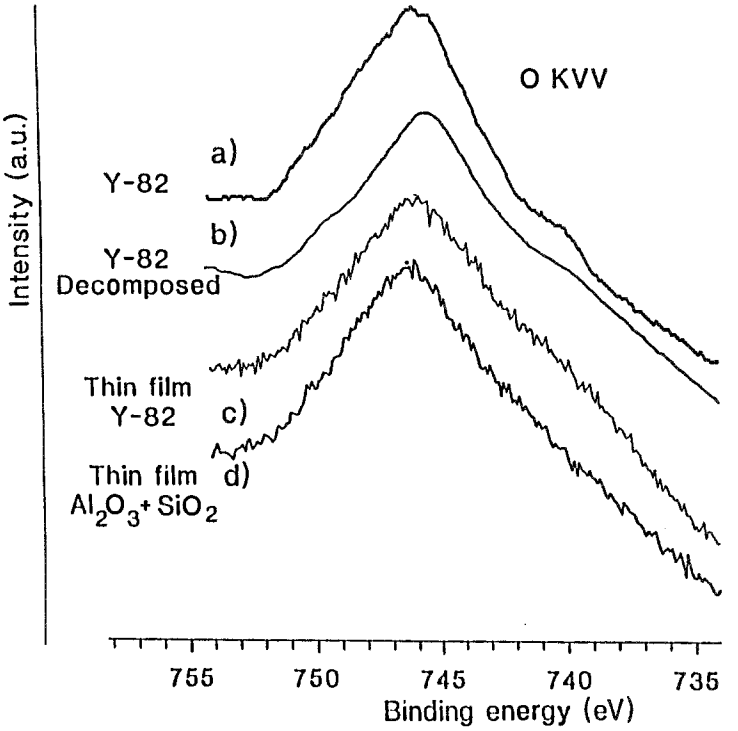

Fig. 6. Oxygen O KVV Auger transitions: a) Y-82 target, b) thermally decomposed Y-82 (1470 K, 10 hours), c) sputter deposited silica alumina film on gold foil using Y-82 as target; and d) sputter deposited silica alumina film on gold foil using a mechanical mixture of SiO_2 and Al_2O_3. (Electron kinetic energy = 1253.6 eV – binding energy.)

silica and alumina thin films and compared their activity to that of the silica-alumina films.

The surface of the films were analyzed by XPS and the trends described in the previous section were reproducible: the chemical composition of the targets and the films were similar. No change in the composition could be observed after 15–20 minutes of deposition.

Cumene cracking is one of the most studied acid catalyzed reaction [11,12]. Corma and Wojciechowski [11] showed that it is not a simple reaction as it was reported in the early acid catalysis literature, and they gave the most comprehensive scheme for the reaction. On zeolites, the primary products are propene, benzene and diisopropyl benzene.

Blank experiments on gold foils (20 cm^2) showed some activity. We could detect the formation of diisopropyl benzenes, benzene, propene and iso-butene at 570 K. The reaction rate was very low, in the order of 10^{10} molecules/min. We found that the adsorption rate of the aromatic products on the glass walls of the reactor was within the same order of magnitude. Since propene did not adsorb on the walls, we chose its rate of formation as the measure of catalytic

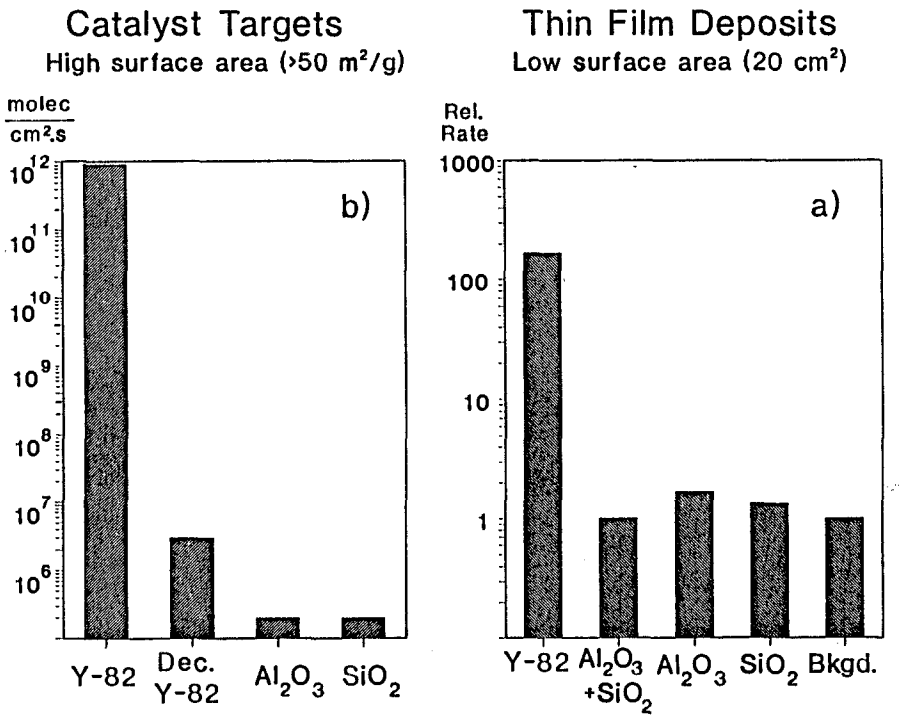

Fig. 7. Initial rate of cumene cracking at 570 K; a) for sputter deposited thin films using Y-82, a mixture of alumina and silica, alumina, silica as targets and the initial rate for the background reactions as well; and b) for high surface area catalysts: zeolite Y-82, decomposed zeolite Y-82 (in He at 1470 K for 10 hrs), alumina and silica.

activity. This choice was further supported by the reaction network developed by Wojciechowski [10,11], because propene is produced only in one primary reaction: the cracking of isopropyl benzene.

In fig. 7a we report the initial reaction rates for cumene cracking for the sputter deposited films. For the 20 cm^2 film deposited using a zeolite target, the activity is clearly measurable and it is about two orders of magnitude higher than the activity of alumina or silica thin films or the activity of the film prepared from a mixture of silica and alumina as target. This implies that the sputter deposited film maintains the chemical memory of the target material. This effect may be due to similar local chemical environments in the amorphous thin film and in the target zeolite and/or some structural similarities yet to be identified. Further studies using a series of different zeolite targets could perhaps provide more definite answers.

In fig. 7b the initial reaction rates of the target materials are given. The high surface area zeolite samples are 6–7 orders of magnitude more active than the high surface area alumina or silica.

4. Conclusions

Using argon ion beam sputter deposition, homogeneous and amorphous thin silica-alumina layers can be prepared on gold foil using zeolite targets. Although initially the Si/Al ratio of the films is larger than that of target and bulk compositions, at the later stages of deposition it approaches the bulk composition of the target. XPS results indicate that the O 1s, Al 2p and Si 2p peak positions and the line shape of the O KVV Auger transition is very similar to the targets. This method seems to be a promising new tool in the preparation of model catalysts.

We have shown that silica-alumina films are active in cumene cracking, but one needs at least 20 cm^2 total geometric surface area to be able to detect it comfortably over that of the background that was prepared by depositing a film of the same thickness from a mechanical mixture of silica and alumina.

Acknowledgements

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