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AN INVESTIGATION OF THE DESORPTION OF HYDROGEN FROM LITHIUM OXIDE
USING TEMPERATURE PROGRAMMED DESORPTION AND DIFFUSE REFLECTANCE
INFRARED SPECTROSCOPY*

by

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MAST

An Investigation of the Desorption of Hydrogen from Lithium Oxide using Temperature Programmed Desorption and Diffuse Reflectance Infrared Spectroscopy

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Abstract

The addition of hydrogen to the purge stream has been shown to enhance tritium release from ceramic breeder materials. In an attempt to determine the mechanism for this enhancement we have investigated the adsorption and desorption of hydrogen and water from lithium oxide (a leading candidate for the breeder material) by temperature programmed desorption and diffuse reflectance infrared spectroscopy. The results from these studies indicate that several different types of hydroxide groups are formed on the lithium oxide surface. They also suggest that under certain conditions hydride species form on the surface. The role of these species in tritium release from lithium oxide is discussed.

Introduction

Lithium oxide is one of the leading candidates for use as a tritium breeding material in a fusion reactor. Many experiments have demonstrated the relative ease of tritium recovery from this material. Tritium release is particularly facile when a purge gas (argon or helium) containing hydrogen, typically at levels of about 0.1%, is used. However, addition of hydrogen to the purge gas has a penalty associated with the tritium purification process. In particular, a large amount of hydrogen in the purge will necessitate a larger tritium purification unit and, therefore, higher costs. Optimizing tritium release while minimizing the amount of hydrogen necessary in the purge gas requires a better understanding of the tritium desorption step and the interactions of hydrogen with the lithium oxide surface.

One method typically used to study surface desorption processes is temperature programmed desorption (TPD). In this technique, a gas is adsorbed on the sample, the sample is then heated at a constant rate, and the gas desorbed from the sample is detected downstream by a technique such as mass spectrometry. From the shape and position of the desorption peak in the TPD spectra one can obtain information about the energetics of the desorption process [1]. A shortcoming is that this technique provides no information on the identity or form of the species that is desorbing from the surface. For example, if a tritium atom exists on a lithium oxide surface, it may be either as a triton (H^+) or as a tritide (H^-). When it desorbs into the gas phase (as HTO or HT) the tritium species now can react with hydrogen or water in the gas phase to form an equilibrium mixture of H_2 , HT, H_2O , and HTO. The mass-spectrometer downstream will only detect the equilibrium mixture and will provide no information about whether the desorbed species was T^+ or T^- , or worse whether the species was being desorbed from the Li_2O sample or

from the support structure. When several peaks are observed in a TPD spectrum, there is no information other than the energetics to help determine what caused the different (different surface species, diffusion and desorption of the same species, desorption from other surfaces). In addition, with several overlapping peaks, it is sometimes difficult to determine the number of peaks present.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) has been used to view hydroxyl groups on the lithium oxide surface [2]. Different infrared absorptions were observed in the OH region, indicating different types of OH groups present on the surface. However, no energetic information was obtained regarding the desorption of these hydroxyl groups. In an effort to gain information about the species present on the surface and their relationship to peaks in the TPD spectra, we have turned to a study of hydrogen adsorption and desorption from lithium oxide by using a combination of TPD and DRIFTS measurements.

Experimental

The TPD measurements were performed using an apparatus described previously [3]. Hydrogen and deuterium were dried by passing the high-purity gas through a commercial deoxygenating unit. Hydrogen (deuterium) was adsorbed on a lithium oxide sample at 250°C for a period from 3 to 24 h. The purge gas was then changed, and the temperature increased linearly while the outlet gas stream was continuously monitored by mass spectroscopy.

The DRIFTS measurements were performed using a Bomem spectrometer equipped with a diffuse reflectance attachment (Harrick Scientific DRA-Praying Mantis). The samples were commercial lithium oxide powder (Alfa) and were contained in a vacuum chamber equipped for diffuse reflectance (Harrick Scientific) with ZnSe windows and an internal heater. Experiments were performed by exposing the sample to Ar+0.1% H_2 or Ar+0.1% D_2 at various temperatures (between 100 and 400°C) and recording the infrared spectra. Kinetic experiments were performed by switching the purge gas (eg. from Ar + 0.1% H_2 to pure Ar or Ar + 0.1% D_2) then recording the spectra at selected time intervals.

Quasi TPD-DRIFTS experiments were performed by exposing the lithium oxide sample to a purge gas containing deuterium, changing the purge stream to one containing hydrogen, then slowly raising the temperature manually from 200 to 400°C while sampling the purge gas downstream of the sample with the mass spectrometer and recording the infrared spectra at discrete times during the temperature increase. To begin, Ar +0.1% D_2 was passed over the sample at 115-120°C for 16 h. The purge gas was then switched to Ar+0.1% H_2 , and the temperature of the sample slowly increased to 400°C. The gas was continuously sampled by mass spectrometry and diffuse reflectance spectra were recorded at specific temperatures during the TPD run: 157, 174, 200, 225, 250, 275, 308, 322, 347, 361, 374, and 395°C.

Results and Discussion

TPD

For TPD experiments into a purge gas of pure argon, one narrow peak was observed for temperature ramps up to 750°C at heating rates of 2, 5, and 10 K/min. For a heating rate of 1 K/min, one peak with what might be a second small peak near the temperature limit of the experiment was observed (Fig 1). The main peak is narrow, and we were unable to obtain a consistent activation energy for this peak by comparing results from line-shape analysis and plots of $\ln(T_m^2/H)$ vs. $1/T_m$ (where T_m is the temperature of the peak maximum and H is the heating rate). The activation energy calculated from the plots of $\ln(T_m^2/H)$ vs. $1/T_m$ is 88 kJ/mol while that obtained from line-shape analysis is about a factor of two higher. This suggests that desorption into pure Ar is not a simple first-order desorption process.

The TPD experiments performed in a purge gas of Ar+0.1% H₂ exhibit more than one peak in the desorption spectra. The main peak occurs at temperatures close to those seen in pure argon; however, additional peaks occur at higher temperatures and at temperatures near the maximum temperature for the experiment (Fig.2). For the main peak plots of $\ln(T_m^2/H)$ vs $1/T_m$ give an activation energy of 102.5 kJ/mol (24.5 kcal/mol); however, line-shape analysis again gives a much higher activation energy for this peak. This suggests that the mechanism for desorption of this species is also not a simple first-order desorption. For the second peak, an activation energy of 73 kJ/mol is obtained from line-shape analysis and plots of $\ln(T_m^2/H)$ vs. $1/T_m$. The other peaks were too close to the temperature limit for the experiment to be able to obtain activation energies by these methods.

Figure 1 TPD spectra for desorption of OD from Li₂O at a heating rate of 1 K/min with a purge gas of pure argon.

Figure 2 TPD spectra for desorption of OD from Li₂O at a heating rate of 1 K/min with a purge gas of Ar + 0.1% H₂

DRIFTS

Figure 3 shows the DRIFTS spectra of a lithium oxide powder after exposure to a purge gas of Ar+0.1%D₂ at 365°C. Several different absorptions are observed for OH and OD. Under different conditions, other peaks appear more prevalent. Deconvolution of these curves indicates four different OH absorptions: 3657, 3604, 3480, and 3400 cm⁻¹. Corresponding OD peaks have been observed at 2695, 2659, and 2560 cm⁻¹ upon exposure to D₂. (The OD peak corresponding to the OH peak at 3400 cm⁻¹ has not yet been observed, probably due to the very low intensity of this OH peak under the conditions investigated.) These results indicate four different OH species on the surface. We propose that these are OH species with coordination numbers of 2, 4, 6 and 8, respectively. The strength of the OH bond and, therefore the OH vibration frequency, will depend on the electron density on the oxygen. As the electron density on the oxygen is reduced by coordination to Li atoms in the lattice the O-H bond strength should decrease, decreasing the frequency of the absorption. This is similar to the effect seen for infrared absorptions of terminal versus bridging carbonyl groups.

Under certain conditions, we have seen infrared absorptions in the region where a Li-H stretch is expected. These infrared absorptions at 1245 to 1212 cm⁻¹ are shifted to slightly lower frequencies than that observed for lithium hydride (1280 cm⁻¹). The hydride absorption in the infrared region was generally seen at temperatures of about 380°C and higher. Confirmation that this absorption is due to a hydride by isotopic substitution with deuterium has not been possible since the deuterium peak would be shifted to a position beyond the absorption edge. However, these absorptions have only been seen in a purge gas containing

Figure 3 Infrared spectra of Li₂O after exposure to a purge gas containing H₂ and D₂ showing multiple OH and OD absorptions.

Figure 4 Hydride region of infrared spectra for Li₂O in a purge gas of Ar + 0.1% H₂ at 395°C

hydrogen. At 395°C with a purge gas of Ar+0.1% hydrogen, an absorption occurs at 1218 cm^{-1} ; when the purge gas is changed to pure argon this peak disappears (compare Figs. 4 and 5), giving a strong indication that this absorption is due to the presence of a Li-H species on the surface. The presence of a Li-H species on the surface suggests that hydrogen is adsorbed on the surface heterolytically to form H^+ (OH^-) and H^- (Li-H). Quantum mechanical calculations indicate that this type of heterolytic adsorption is expected on some lithium oxide surface [4].

Preliminary kinetic studies have been performed. The decomposition of the hydroxyl species was followed at 400°C by recording the spectra at about 10-min intervals (see Fig. 6). The preliminary data for the decomposition of the main peak at 3657 cm^{-1} appear consistent with a first order desorption which is an order of magnitude slower than that reported for the decomposition of bulk LiOH; however, more data are needed. The decompositions of the secondary peaks do not appear to follow first-order processes. Before they start to decay, the secondary hydroxyl peaks tend to remain constant until the peak at 3657 cm^{-1} has decayed substantially. This complicated kinetics may be the reason for the difficulty interpreting the sharp peaks seen in the TPD curves and requires more study.

DRIFTS-TPD

As part of a preliminary study to determine the applicability of a combined TPD-DRIFTS experiment, a quasi TPD experiment was performed while the diffuse reflectance infrared spectra were recorded at discrete times during the temperature increase. Limitations in the apparatus relegated the experiment to a maximum temperature of 400°C and resulted in a heating ramp which was not quite linear, so no

Figure 5 Hydride region of infrared spectra for Li_2O in a purge gas of pure argon at 400°C

Figure 6 Hydroxyl region of infrared spectra of Li_2O in Ar + 0.1% H_2 at 0, 20, 30 and 40 min after a temperature increase to 400°C

quantitative information regarding the activation energies could be obtained. However, the results do provide some qualitative findings and indicate that the technique of combined TPD-DRIFTS should be pursued further. The pressure-time curve for mass 18 during the temperature ramp is shown in Fig. 7; identical curves were obtained for mass 17 and 19. The infrared spectra show no changes until after the desorption peak has started in the TPD. While the desorption peak is rising in the TPD, the OH absorption intensity decreases at 3657 cm^{-1} . After the TPD peak has reached its maximum, the OH peak at 3657 cm^{-1} has disappeared (Fig. 8, 395°C curve). At this point, a Li-H peak is seen in the infrared spectra (Fig. 9, 395°C curve).

The combination of the TPD curve and the DRIFTS results suggests that the TPD peak observed at about 390°C (663 K) is due mainly to removal of the OH species at 3657 cm^{-1} from the surface. The observation of this species at the surface and the observed change in the concentration of this species with time indicate that the

Figure 7 Time dependence of mass 18 peak for desorption from Li_2O during a temperature increase from 250 to 400°C .

Figure 8 Hydroxyl region of infrared spectra during temperature increase from 250 to 400°C

Figure 9 Hydride region of infrared spectra during temperature increase from 250 to 400°C

rate-controlling mechanism for the disappearance of this peak is not bulk diffusion. If bulk diffusion were the rate controlling process, one would expect the surface concentration to be near zero and no appreciable change in the surface concentration of this species would be observed during the TPD peak. The combination of the TPD and DRIFTS also indicates that the hydride species is not observed until the OH species at 3657 cm^{-1} is absent. One possible explanation is that these hydroxide groups occupy the sites at which H^- adsorbs.

Conclusions

Our studies indicate that four different types of hydroxyl groups can be observed on a lithium oxide surface. The particular species present vary depending on the temperature and hydrogen pressure of the system. Under some conditions where hydrogen is present in the purge gas, surface hydride species have been observed. This suggests heterolytic adsorption of hydrogen. These studies also indicate that the combination of TPD and DRIFTS could be a valuable method for studying surface processes. This combination overcomes the shortcomings of the individual methods and allows one to determine correlations between species observed on the surface and those detected in the gas phase downstream.

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