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Spectroscopic studies of oxidation of coke in glow discharges in He-O_2, Ar-O_2, and N_2-O_2 gas mixtures

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Abstract

Glow discharges in several different gas mixtures including N_2-O_2, He-O_2 and Ar-O_2 mixtures with different compositions were investigated to study the decoking of coked catalysts. Compared to a glow discharge in pure O_2, the He-O_2 and Ar-O_2 gas mixtures were found to provide significant enhancements in the decoking process, while the N_2-O_2 gas mixture provided only marginal enhancement. The Ar-O_2 gas mixture was found to be particularly effective.

Introduction

We have recently reported the use of a glow discharge in oxygen to investigate 'decoking' of a zeolite catalyst [1]. The process involves dissociation of O_2 in a glow discharge thereby creating O atoms. Subsequent reactions of O atoms with coke lead to the formation of CO, CO_2 and other gaseous products that could be easily pumped out. This paper reports the effect of different gas mixtures including N_2-O_2, He-O_2 and Ar-O_2 mixtures with different compositions to study possible enhancements in the decoking process. Ar-O_2 gas mixture was found to be particularly effective.

Experimental details

The experimental set up has been described in a previous paper [1]. Briefly, it consisted of a cross-shaped discharge cell with adjustable gap between the electrodes. The light emitted by the discharge could be collected through one of the two side ports of the cell for the purpose of monitoring and analysis. The cell was first evacuated to pressures of the order of 10^{-3} mbar and then filled to the appropriate pressure of the oxygen-containing gas mixture under carefully controlled conditions.

A small amount of 'coked' catalyst was spread evenly inside a ceramic boat essentially as a single layer and placed in the discharge cell. This was exposed to the discharge for known times using a periodic-purge mode where the gaseous products were pumped out after regular intervals of time, usually three minutes, and fresh gas mixture was added [1]. The sample was subsequently analyzed to record changes in the carbon content of the catalyst using XPS analysis.

A scanning monochromator coupled to a thermoelectrically cooled photomultiplier was used to monitor the population densities of O atoms, and CO and CO_2 molecules in real time from the spectrally resolved light emitted by the discharge. In particular, for the atomization of O_2, the $3s^5S - 3p^5P$ multiplet of O atoms around 772-775 nm was used [1,2]. For CO, the band heads at 451.1 and 519.8 nm belonging to the $B^1\Sigma$-$A^1\Pi$ bands of the Angstrom system [1,3] were used. For CO_2, however, the band head at 353.4 nm belonging to the $A^2\Pi_{3/2u} - X^2\Pi_{3/2g}$ system of CO_2^+ was used [3]. Furthermore, X-ray photoelectron spectroscopy (XPS) analysis was used to determine the extent of decoking.

Results and discussion

Figure 1 shows the overall yield of O-atoms measured from the intensity of emission on the reference transition using different Ar-O_2, He-O_2, and N_2-O_2 mixtures as a function of O_2 fraction. The pressure in all these cases was .1.4 mbar. While all mixtures show their respective maximum atomization for different O_2 partial pressures, higher yields of O-atoms are recorded when the partial pressure of O_2 is much smaller (≤3%) in the case of Ar-O_2 and He-O_2 gas mixtures. However, the total yield in the case of He-O_2 mixture remains lower than the corresponding Ar-O_2 mixture for similar O_2 contents of the gas mixture. On the other hand, in the case of N_2-O_2 mixture, the maximum yield is obtained when the N_2 component in the mixture is much smaller (≤3%). Furthermore, the total yield of O-atoms in the case of N_2-O_2 mixture remains much lower than the case of Ar-O_2 and He-O_2 mixtures. This may be due to the fact that Ar and He do not react with O-atoms, while both N_2 and N could react with O atoms forming complexes such as NO, NO_2, N_2O, N_2O_5 etc.

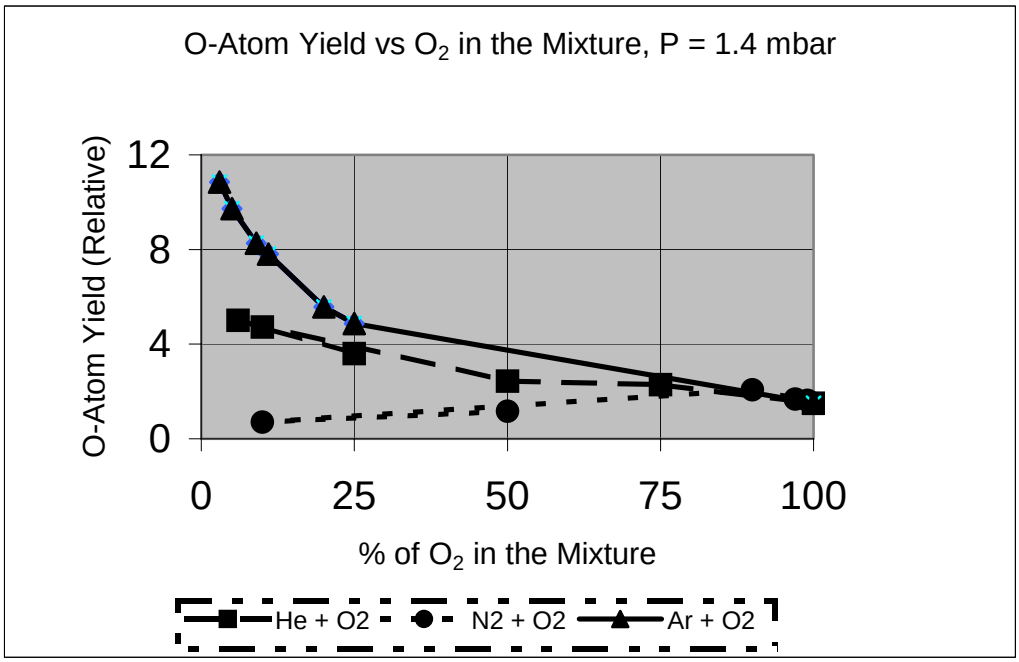

Fig.1: Yield of O-atoms with different compositions of Ar-O_2, He-O_2 and N_2-O_2 gas mixtures as a function of O_2 fraction.

The most important question in the context of decoking is whether or not enhanced atomization of O_2 actually leads to more efficient decoking. In the present paper, we used the net CO yield monitored from the intensity of the band heads at 451.1 and 519.8 nm belonging to the $B^1\Sigma$-$A^1\Pi$ bands of the Angstrom system as indicators of enhanced decoking.

We investigated the cumulative CO emission in three-minute intervals from the catalyst samples exposed to glow discharges in pure O_2 as well as in the Ar-O_2 and He-O_2 gas mixtures. Fig. 2 is a bar graph showing a comparison of the overall yields of CO gas as a measure of decoking. The XPS analysis of the carbon content of the catalyst samples exposed to the discharges also confirmed the above results. Under the experimental conditions discussed here, the mixture of choice seems to be the Ar-O_2 mixture with only a few percent of O_2.

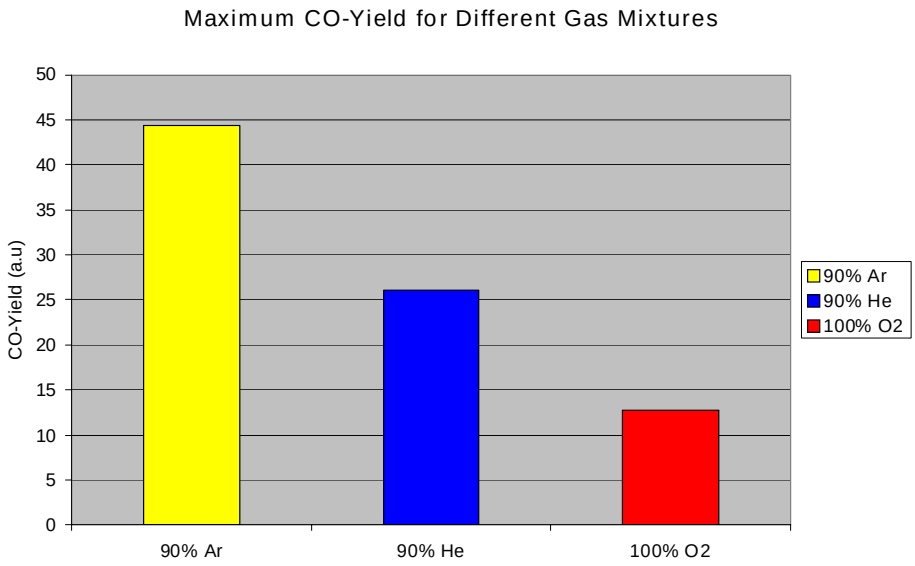

Fig. 2: Bar graph showing the maximum yield of CO for different gas mixtures but at low pressures around 0.3 mbar.

Conclusions

Using spectroscopic measurements, we have demonstrated that a significant increase in the yield of O atoms and the accompanying yield of CO is possible using different gas mixtures including N_2-O_2, He-O_2 and Ar-O_2 in a glow discharge. The Ar-O_2 gas mixtures with small amount of O_2 were seen to give the best results for decoking.

Acknowledgements

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