Spectroscopic studies of oxidation of coke in glow discharges in He-O\textsubscript{2}, Ar-O\textsubscript{2}, and N\textsubscript{2}-O\textsubscript{2} gas mixtures

M. A. Khan\textsuperscript{1} and A. A. Al-Jalal\textsuperscript{2}

1. Laser Research Section, Center for Applied Physical Sciences, The Research Institute
   King Fahd University of Petroleum and Minerals
   Dhahran 31261, Saudi Arabia

2. Department of Physics
   King Fahd University of Petroleum and Minerals
   Dhahran 31261, Saudi Arabia

Abstract

Glow discharges in several different gas mixtures including N\textsubscript{2}-O\textsubscript{2}, He-O\textsubscript{2} and Ar-O\textsubscript{2} mixtures with different compositions were investigated to study the decoking of coked catalysts. Compared to a glow discharge in pure O\textsubscript{2}, the He-O\textsubscript{2} and Ar-O\textsubscript{2} gas mixtures were found to provide significant enhancements in the decoking process, while the N\textsubscript{2}-O\textsubscript{2} gas mixture provided only marginal enhancement. The Ar-O\textsubscript{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\textsubscript{2} in a glow discharge thereby creating O atoms. Subsequent reactions of O atoms with coke lead to the formation of CO, CO\textsubscript{2} and other gaseous products that could be easily pumped out. This paper reports the effect of different gas mixtures including N\textsubscript{2}-O\textsubscript{2}, He-O\textsubscript{2} and Ar-O\textsubscript{2} mixtures with different compositions to study possible enhancements in the decoking process. Ar-O\textsubscript{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\textsubscript{2} molecules in real time from the spectrally resolved light emitted by the discharge. In particular, for the atomization of O\textsubscript{2}, the 3s\(^5\)S –3p\(^5\)P 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 \(B^1Σ^+ A^1Π\) bands of the Ångstrom system [1,3] were used. For CO\textsubscript{2}, however, the band head at 353.4 nm belonging to the \(A^2Π_{3/2u} – X^2Π_{3/2g}\) system of CO\textsubscript{2}\textsuperscript{+} 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\textsubscript{2}, He-O\textsubscript{2}, and N\textsubscript{2}-O\textsubscript{2} mixtures as a function of O\textsubscript{2} fraction. The pressure in all these cases was .1.4 mbar. While all mixtures show their respective maximum atomization for different O\textsubscript{2} partial pressures, higher yields of O-atoms are recorded when the partial pressure of O\textsubscript{2} is much smaller (≤3\%) in the case of Ar-O\textsubscript{2} and He-O\textsubscript{2} gas mixtures. However, the total yield in the case of He-O\textsubscript{2} mixture remains lower than the corresponding Ar-O\textsubscript{2} mixture for similar O\textsubscript{2} contents of the gas mixture. On the other hand, in the case of N\textsubscript{2}-O\textsubscript{2} mixture, the maximum yield is obtained when the N\textsubscript{2} component in the mixture is much smaller (≤3\%). Furthermore, the total yield of O-atoms in the case of N\textsubscript{2}-O\textsubscript{2} mixture remains much lower than the case of Ar-O\textsubscript{2} and He-O\textsubscript{2} mixtures. This may be due to the fact that Ar and He do not react with O-atoms, while both N\textsubscript{2} and N could react with O atoms forming complexes such as NO, NO\textsubscript{2}, N\textsubscript{2}O, N\textsubscript{2}O\textsubscript{3} etc.
The most important question in the context of decoking is whether or not enhanced atomization of O\textsubscript{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\textsubscript{2} as well as in the Ar-O\textsubscript{2} and He-O\textsubscript{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\textsubscript{2} mixture with only a few percent of O\textsubscript{2}. 

Fig.1: Yield of O-atoms with different compositions of Ar-O\textsubscript{2}, He-O\textsubscript{2} and N\textsubscript{2}-O\textsubscript{2} gas mixtures as a function of O\textsubscript{2} fraction.
**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.

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References

