Surface adsorption and reaction between enolic species and nitrate on Ag/Al₂O₃ for HC-SCR

Deng, H. Yu Y.B. and He H.*
State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
* Corresponding author: honghe@rcees.ac.cn

Introduction
NOx removal from lean-burn exhaust remains a major challenge in environmental catalysis. Selective catalytic reduction of NOx by hydrocarbons (HC-SCR) is a potential method to remove NOx from lean-burn exhausts. The alumina-supported silver catalyst (Ag/Al₂O₃) is deemed to be one of the most effective materials for HC-SCR of NOx in excess oxygen [1]. In particular, ethanol is extremely effective for the SCR of NOx over Ag/Al₂O₃. Isocyanate species (-NCO) are widely accepted as a vital intermediate when hydrocarbons and oxygenated hydrocarbons are used as reducing agents. Isocyanate species may arise from the thermal decomposition of a precursor complex, NOxCyHz, during reduction of NOx by hydrocarbons. Concerning the formation of -NCO species, a mechanism is proposed whereby NO+O₂+CxHy (hydrocarbons)→NOx (such as nitrates) + CxHyOz (such as acetate and enolic species) → R-NO₂ + R-ONO → -NCO + -CN [2]. In particular, nitrates and enolic species could be key precursors in the formation of -NCO during NOx reduction by oxygenated hydrocarbons [3]. However, the chemical structures and features of R-NO₂ or R-ONO on the surface of Ag/Al₂O₃ are little reported.

In this study, In situ DRIFTS studies of NO oxidation and partial oxidation of ethanol were performed on the surface of Ag/Al₂O₃ catalysts, respectively. The intermediate species were identified. With the aid of DFT calculation, the nitrates and oxidized hydrocarbon intermediates species were modeled. Furthermore, the reaction products between enolic species and nitrates were simulated to anticipate the corresponding chemical roles.

Materials and Methods
Ag/Al₂O₃ catalysts with constant loadings (2 wt % loading) were prepared by an impregnation method. In situ DRIFTS spectra were recorded on a Nexus 670 FT-IR (Thermo Nicolet), equipped with an in situ diffuse reflection chamber and a high sensitivity MCT/A detector. All DFT calculations were performed using Materials Studio (MS) Modeling CASTEP from Accelrys. Periodic boundary conditions in the Generalized Gradient Approximation (GGA) were applied using the Perdew-Wang (PW91) function in our cases. All initial parameters had been checked by convergence tests. The electron-ion interaction was described by the ultrasoft potential in reciprocal space. A tight convergence of the plane-wave expansion was obtained with a kinetic energy cut-off of 400 eV.

Results and Discussion
Exposure of Ag/Al₂O₃ to the feed gas (C₂H₅OH+O₂) resulted in the appearance of predominant peaks (1633, 1410, and 1336 cm⁻¹), which can be assigned to adsorbed enolic species (as shown in Figure 1). After adsorption of NO+O₂ on Ag/Al₂O₃, both monodentate (1560, 1250 cm⁻¹) and bidentate NO₃⁻ (1585 and 1298 cm⁻¹) could be found [4]. The surface-adsorbed intermediate structures were constructed by DFT theoretical methods. Silver ion sites [5] rather than Al³⁺ ions on the surface were the favorite sites for the adsorption of enolic or nitrate species separately. The total energies are listed in Table 1. However, enolic species are more closely bonded with silver sites when both adsorbed species compete with each other on Ag ion sites.

<table>
<thead>
<tr>
<th>Table 1. The total energies for different adsorption models</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Energy (eV)</td>
</tr>
<tr>
<td>Enolic species</td>
</tr>
<tr>
<td>Nitrate</td>
</tr>
<tr>
<td>Enolic species (Ag) + Nitrate (Al)</td>
</tr>
<tr>
<td>Enolic species (Al) + Nitrate (Ag)</td>
</tr>
<tr>
<td>Enolic species (Ag) + Nitrate (Ag)</td>
</tr>
</tbody>
</table>

The reaction between adsorbed enolic species and nitrate may take place right on silver ion sites. Therein, surface models of CH₃NO₂ and/or CH₃ONO were simulated to understand the process.

Significance
A surface model of enolic species and nitrate on the Ag/Al₂O₃ catalyst was constructed based on experimental results. The reaction between them was explored at the molecular level.

Figure 1. In situ DRIFTS spectra of adsorbed species on Ag/Al₂O₃ catalyst in a flow of C₂H₅OH+O₂ and NO+O₂ respectively, and corresponding surface models.

References