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Nano-structural investigation of Ag/Al_2O_3 catalyst for selective removal of O_2 with excess H_2 in the presence of C_2H_4

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ABSTRACT

$Ag/\gamma\text{-}Al_2O_3$ catalysts have been characterized in-depth during different thermo-chemical treatments by *in situ* diffuse reflectance UV–visible spectroscopy and *quasi in situ* Transmission Electron Microscopy. The combination of these techniques indicates that sintering and redispersion of silver is clearly observed from the increases and decreases in the absorption band intensity over the range of 250–600 nm due to the presence of silver clusters and silver nanoparticles. These results allow us to study the effect of the reaction feed on the metal dispersion at different operation conditions and discuss the formation of active sites during the selective catalytic reduction of O_2 with excess H_2 in the presence of unsaturated hydrocarbons. In this case high catalytic activity and selectivity toward the oxygen removal was achieved for this catalyst.

1. Introduction

Silver based catalysts have been used widely in many reactions such as selective oxidation of organic compounds (e.g. ethene, propene and methanol), ammonia and hydrocarbon selective catalytic reduction (SCR) of NO_x and the selective hydrogenation of aldehydes [1–3]. In addition, $Ag/\gamma\text{-}Al_2O_3$ was recently found to selectively remove trace amounts of oxygen with the excess hydrogen in the presence of a wide range of unsaturated hydrocarbons without causing either oxidation or reduction of the hydrocarbon [4]. Depending on the reaction of interest, the silver catalyst may be utilised in the presence of excess oxygen or hydrogen leading to structural differences and, therefore, structural characterization of the silver catalyst under those conditions may help understanding its catalytic behaviour.

Recently, diffuse reflectance UV–visible spectroscopy (DRUVS) has attracted much attention for the investigation of silver speciation heterogeneous catalysts. Shibata et al. [5–7] used the UV–vis techniques to study silver catalysts under SCR reaction conditions in the absence and presence of H_2. The catalyst was found to contain mainly Ag^+ in the absence of H_2 in SCR feed whereas the presence of small silver clusters ($Ag_n^{\delta+}$, $2 < n < 4$) was observed once <1% of H_2 was added into the feed. With higher H_2 concentration (>1%), the formation of metallic silver cluster (Ag_m, $3 < n < 5$) was observed. According to the UV–vis results together with EXAFS study, the authors proposed that $Ag_n^{\delta+}$ clusters are responsible for the high activity of silver based catalyst in SCR-NO_x reduction. Some differences from this study were observed by Breen et al. using octane as the reductant. *In situ* EXAFS showed that the silver clusters formed in the absence of hydrogen and under carbon monoxide but the general conclusion that silver clusters were highly active for SCR-NO_x reduction was also demonstrated which is consistent with the EXAFS results [8]. Richter et al. [9] also used DRUVS in order to study the silver species present under reduction and oxidation reaction conditions in the temperature range of 250–550 °C. In their study, the presence of absorption bands due to silver crystallites (~400 nm) were found in the reduced 1% Ag/Al_2O_3 catalyst whereas a decrease in the absorption intensity in this range was observed in the reoxidized sample. The results clearly suggest reversible transformation of silver species under reduced-oxidized atmospheres.

In our study, structural investigation of $Ag/\gamma\text{-}Al_2O_3$ catalyst under redox reaction conditions has been investigated with the use of DRUVS and TEM techniques. Although the DRUVS technique has some limitations in quantitative analysis, it is very simple to operate and provides useful information concerning the oxidation

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state of silver, size of silver clusters and the presence of isolated Ag^+ species. Good correlation between the UV–vis results and TEM studies were obtained. These two techniques were used to investigate the silver active sites present in the Ag/γ-Al_2O_3 catalyst during the selective reduction of oxygen by hydrogen in the presence of hydrocarbons. This reaction is important in order to purify ethene, when used as a monomer for the production of polyethene. Trace amounts of oxygen deactivate the polymerisation catalyst and thus reduce the product yield [10]. Therefore, a catalyst which reduces the oxygen with hydrogen present whilst preventing hydrogenation or oxidation of the unsaturated hydrocarbon is important and silver based catalysts have been shown to have extremely high selectivities at high conversion [4].

2. Experimental

2.1. Material synthesis

The catalyst was prepared by incipient wetness impregnation of a commercial γ-alumina support (Saint-Gobain) at room temperature using silver nitrate (Riedel-de-Haën) as the metal precursor. The appropriate amount of metal precursor was dissolved in distilled deionised 18.2 MΩ water, and then added to the support. The solid was then dried at 80 °C (12 h) and subsequently calcined at 630 °C (6 h). The final Ag loading of the catalyst was 1.4 wt.%, as determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The BET surface of the support was 216 m^2/g and a value of 7.8 nm was obtained for the average pore size according to the BJH (The Barrett–Joyner–Halenda) method. After impregnation the surface area and the average pore size slightly decrease to 212 m^2/g and 7.4 nm, respectively.

2.2. Characterization techniques

Diffuse reflectance ultraviolet–visible spectroscopy measurements were performed using a Lambda 650S UV–vis spectrophotometer equipped with a Harrick high temperature reaction chamber and an integrating sphere detector. This chamber allows us to control the gas mixture flow and the temperature, giving the opportunity to study the catalyst under different chemical environments such as the reaction mixture. MgO and γ-Al_2O_3 were used as background spectra for γ-Al_2O_3 and Ag/γ-Al_2O_3 samples, respectively.

High Resolution Transmission Electron Micrographs were collected on a 200 kV JEOL JEM-2010F instrument with a structural resolution of 0.19 nm at Scherzer defocus conditions. Scanning Transmission Electron Microscopy (STEM) images were recorded in the same instrument using a high angle annular dark field (HAADF) detector and an electron beam probe of 0.5 nm to determine the particle size distribution and the metal dispersion assuming a cubooctaedric shape. This analysis was performed counted up to 350 particles. A titration of the Ag surface sites by the traditional chemisorption methods was not carried out because those typically involve oxidative and/or reductive pre-treatements that are likely to alter the shape and size of silver particles (as shown by our work) and therefore the corresponding dispersion. The pre-reduced catalysts were pre-treated in a U-shape quartz reactor with two valves that permit the transfer of the sample to a glove box (855 AC, Plas labs Inc.) where the sample was mounted on a copper grid by a dry method to prevent sample from contacting with any solvent. A high resolution vacuum transfer holder (VTST4006, GATAN ltd.) was used to transfer the sample to the microscope. In the case of the fresh and reoxidized samples a standard single tilt holder was used.

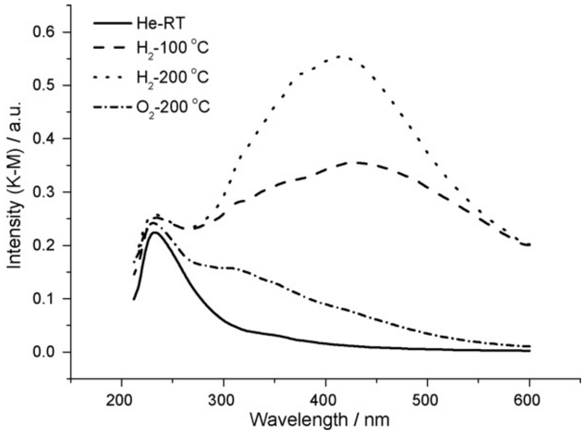

Fig. 1. *In situ* UV–Vis DRS spectra of Ag/γ-Al_2O_3 recorded during different consecutive thermo-chemical treatments: Helium at room temperature, 5% H_2/He at 100 and 200 °C and under 5% O_2/He.

2.3. Catalytic tests

The catalytic tests were conducted at ambient pressure using stepwise isotherms between room temperature and 250 °C with 50 °C interval. The heating ramp rate used was 2 °C/min and the time on stream at each reaction temperature was 50 min. The reactor effluents were analysed by on-line gas-chromatography using a gas chromatograph fitted with packed columns (molecular sieve, Chromosorb B and Haysep A, N and T) and TCD and FID detectors. Initial results were obtained using simplified feed 0.2% O_2, 38.5% H_2 and 18% C_2H_4 and helium balance. The catalyst amount and the gas hourly space velocity were 50 mg and 20000 h^{-1}, respectively. The catalyst was also tested using representative industrial feed conditions for the ethene polymerisation. In this case, the feed was set to 38.5% H_2, 18% C_2H_4, 0.2% O_2, 4.8% CO, 2% CO_2, 0.14% 1,3-butadiene, 0.15% C_2H_2 and helium balance.

3. Results and discussion

In situ UV–vis DRS experiments were used to investigate silver species present under well controlled conditions. Fig. 1 summarizes the results obtained for the fresh sample and after exposure to subsequent reducing and oxidizing atmospheres, showing a dramatic change in the spectra under different environments. It should be noted that γ-Al_2O_3 support exhibits an absorbance in the region of 208–308 nm with its maximum intensity at 230 nm (Supplementary data, Fig. 1SI). This band corresponds to ligand to metal charge transfer transitions [11] from O^{2-} to Al^{3+}. Since γ-Al_2O_3 absorbed light in the similar region as silver ions, γ-Al_2O_3 support has been used as reference background for Ag/γ-Al_2O_3 catalyst.

The fresh sample, i.e. calcined at 630 °C without pre-reduction, shows an absorption maximum at 233 nm with tail extending to ~420 nm. The absorbance in the region below 250 nm is generally attributed to electronic transitions [12–14] from $4d^{10}$ to $4d^9\,5s^1$ of highly dispersed Ag^+ ions. However, on the basis of the selection rules this electronic transition is forbidden, therefore, the intense absorption observed in this case is more likely to be due to a charge transfer transition from O^{2-} to Ag^+. The absorption band in the range of 250–390 nm is commonly ascribed to silver clusters ($Ag_n^{\delta+}$ with $n \leq 8$) with a variety of cluster sizes and/or different oxidation states [15,9]. Therefore, the broad absorptions above 250 nm observed for the sample were tentatively assigned to the presence of $Ag_n^{\delta+}$ clusters and silver nanoparticles with various sizes and/or oxidation states. It should be noted that in contrast with the X-Ray diffraction (XRD) and conventional TEM, the existence of silver