SURFACE ACIDITY AND PROPETIES OF TiO_2/SiO_2 CATALYSTS PREPARED BY ATOMIC LAYER DEPOSITION: DRIFTS, VISIBLE RAMAN SPECTROSCOPY STUDIES

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INTRODUCTION

TiO_2-SiO_2 mixed oxides are important industrial materials of great interest either as a catalyst or as a support for active species. Significant progress has been made in understanding their physical and chemical properties, while the mechanism of their acidity is still debated. Notari et al. (Catalysis Today 116 (2006) 99-110) summarized the literatures on this subject. Briefly, their work provided evidence that high purity TiO_2-SiO_2 mixed oxides do not have Brønsted acid sites, which conflicted with previous studies in 1990s, such as Tanabe (1), Ko (2), Liu (3), Doolin (4). Notari et al. explained that the discrepancy with previous results was very likely due in some instances to the presence of acid-inducing impurities in materials used in early works and in others to the fact that methods used to detect Brønsted acidity.

In the present work, we use Atomic layer deposition (ALD) technique, which can precisely control the deposition amount, to grow TiO_2 on silica gel with titanium tetrachloride and titanium isopropoxide, two types of metal precursors. The acidity and properties of these TiO_2/SiO_2 catalysts were further investigated by DRIFTS and visible (488 nm) Raman spectroscopy using pyridine as probe molecule at room temperature.

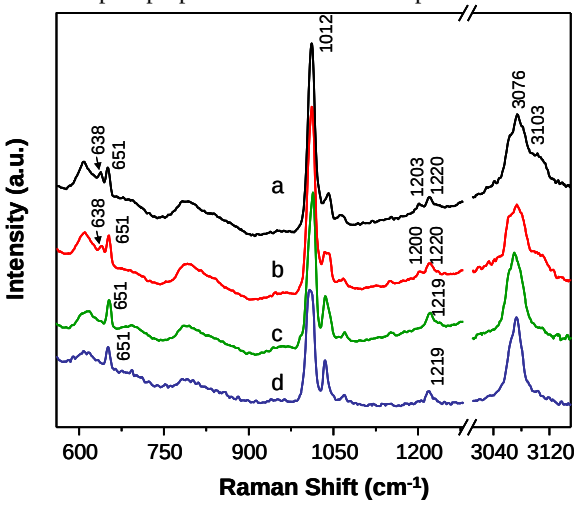
EXPERIMENTAL

The TiO_2 ALD on silica gel was performed using a viscous flow reactor as described previously (5, 6).The TiO_2 films were deposited at temperature of 150-300°C using alternating exposure to titanium tetrachloride ($TiCl_4$, Sigma-Aldrich, 99%) and Millipore water with dose time of 50 sec and purging time of 150 sec, where the $TiCl_4$ and water were both kept at room temperature. For comparison, titanium isopropoxide (TTIP, Sigma-Aldrich, 97%) metal precursor was also used. In this case, the TTIP metal precursor source was heated to 100°C to get reasonable dose time due to its lower vapor pressure. In parallel, the inlet line was heated to 140°C to prevent TTIP condensing on the inner wall of the inlet lines. The TiO_2 films prepared with TTIP were deposited at temperature of 150°C with TTIP dose time 60 sec, and water 120 dose time sec, pure time 240 sec. For both cases, the ultrahigh purity (99.999%) nitrogen was used as carrier gas at a flow rate of 360 sccm and a pressure at 1.3 Torr.

Pyridine adsorption on TiO_2/SiO_2 catalysts was investigated in-situ by DRIFTS and visible (448 nm) Raman spectroscopy at room temperature. In the later case, a mass of 100 mg of catalysts were put into a fluidized bed reactor designed in our lab. Before pyridine adsorption, the TiO_2/SiO_2 sample was purged for 30 min. After saturation, the TiO_2/SiO_2 sample was continued to purge for 30 min to remove most weakly bonded physisorbed pyridine.

RESULTS

The as prepared TiO_2/SiO_2 samples with $TiCl_4$ metal precursor show both Brønsted and Lewis acid sites (seen in figure a, b). However, the Brønsted acid sites have been found to be related to chlorine contamination, which could be removed either by wet nitrogen purging (c in the figure) or calcinations in the air at 450°C (d in the figure). Three new pronounced features at 638, 1200 and 3103 cm^{-1} in Raman spectra are assigned to pyridinium ions. These results provide strong evidence that these two bands, ν6b and ν9a, could be used to detect whether Brønsted acid sites are present on the catalysts, even though, ν6b and ν9a have small Raman scattering cross section, compared with the two ring breathing modes near 1000 cm^{-1} and CH stretching mode 3000 cm^{-1} shift. These conclusions were further conformed by DRIFTS studies and the TiO_2/SiO_2 ALD samples prepared with TTIP metal precursor.



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