IR Observation of Hydrogen Adsorption on Active and Inactive Pt/SO_4^{2-}–ZrO_2

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The formation of H_2O and OH groups on an active Pt/SO_4^{2-}–ZrO_2 (Pt/SZ) catalyst was observed upon hydrogen adsorption at 523 K, whereas only OH groups were formed on an inactive Pt/SZ catalyst.

Pt/SO_4^{2-}–ZrO_2 (Pt/SZ) exhibits high activity and stability for *n*-butane isomerization to isobutane, one of the most important reactions in the petroleum refining industry, at low temperature and in the presence of hydrogen.[1] However, the acidity and acid strength of SO_4^{2-}–ZrO_2 and Pt/SZ have yet be convincingly unresolved. Considerations on this topic include the degree of dehydration of SZ and Pt/SZ, which is regarded as an important factor in these reactions as having a strong influence on the acidity and ratio of Brønsted acid sites to Lewis acid sites of the catalyst;[2] the presence of the right amount of water, a characteristic of the most active catalysts; and the role of hydrogen. Recently, Satoh et al.[3] reported on hydrogen chemisorption over Pt/SZ. They found that the hydrogen uptake on Pt/SZ was very high above 473 K, far exceeding the H/Pt unity ratio (1:1). This phenomenon can be well explained by hydrogen spillover from Pt to the support. Hattori[4] proposed that H_2 adsorption on Pt/SZ can be divided into four steps: 1) dissociation of molecular H_2 on Pt to form H atoms, 2) spillover of H atoms from Pt to the support, 3) migration of the spilled-over hydrogen on the support to Lewis acid sites, and 4) extraction of electrons from H atoms by Lewis acid sites to form acidic protons and hydrides. However, there is at present no direct evidence to support the formation of these species. As research toward obtaining a better understanding of the hydrogen adsorption behavior on Pt/SZ and the effect of coexisting water, the adsorption of hydrogen on active and inactive (with respect to *n*-butane isomerization) Pt/SZ samples at different levels of dehydration was studied by in-situ Fourier transform infrared (FTIR) spectroscopy.

Pt/SZ was prepared according to the procedure reported previously.[3] The surface area of the as-prepared sample was 118 m^2/g, with Pt and sulfur content of 0.5 and 1.9 wt%, respectively. The Pt/SZ catalyst was pressed into a self-supporting wafer (ca. 20 mg/cm^2) and placed in the center of a quartz IR cell connected to a closed gas-circulation system. The catalyst was pre-reduced with H_2 at 573 K for 2 h, followed by evacuation at 573 (hereafter Pt/SZ300) or 723 K (hereafter Pt/SZ450) for 2 h. Pt/SZ300 exhibited a high activity for *n*-butane isomerization (the active catalyst), whereas Pt/SZ450 completely lost activity (the inactive catalyst).[5] The X-ray diffraction (XRD) and elemental analysis revealed that both the catalysts had a tetragonal crystal phase with a trace monoclinic phase and similar sulfur content. Therefore, the remarkable difference in activity is considered to be related to the different degrees of dehydration rather than crystallographic or elemental differences. For H_2 adsorption, H_2 (100 Torr) was introduced into the sample chamber at desired temperatures after purification by passage through a liquid-nitrogen trap for at least 30 min. All the IR spectra were recorded on a JASCO WS/IR-7300 spectrometer with a mercury cadmium telluride (MCT) detector. In most cases, 64 scans at 4 cm^{-1} resolution were collected. Unless otherwise indicated, IR spectra given here are differential, obtained by subtracting the background spectra prior to hydrogen adsorption.

The as-observed background spectra of Pt/SZ300 and Pt/SZ450 prior to H_2 adsorption are given for reference in Figs. 1a and b, being very similar to those of nonloaded SZ300 and SZ450 (not shown). In the high-frequency region (4000–2800 cm^{-1}), terminal and bridging zirconium OH groups were observed at 3743 and 3647 cm^{-1}, respectively, which occur at lower frequencies than in the spectrum of pure ZrO_2,[6] (3774 and 3672 cm^{-1}). This shift is attributed to inductive surface effect due to the presence of charge-withdrawing sulfates on the Pt/SZ samples.[7] For Pt/SZ300, a broad band was observed at 2800–3600 cm^{-1}, and a very weak band appeared at 1620 cm^{-1}. These bands can be attributed to hydrogen-bonded OH groups and traces of strongly bound (adsorbed) water, indicating that water cannot be totally removed from Pt/SZ300. In contrast, the H-bonded species were almost completely nonexistent on Pt/SZ450. In the low-frequency region (1500-800 cm^{-1}), the spectra of both Pt/SZ300 and Pt/SZ450 are complex yet very similar. A strong band at 1368–1400 cm^{-1} is attributed to the S=O stretching mode, and the broad band at 1006 cm^{-1} is correlated with the S–O stretching vibration of sulfate groups.[8,9]

Figures 1c and d show the IR spectra of H_2 adsorption on Pt/SZ300 and Pt/SZ450 at 523 K. The formation of OH groups was clearly observed after adsorbing H_2 onto the active sample at

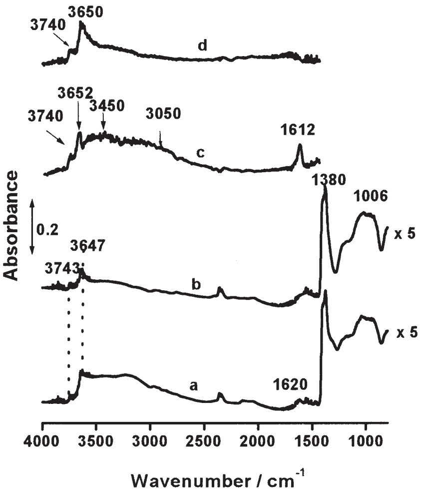

Figure 1. IR spectra of H_2 adsorbed on (c) Pt/SZ300 and (d) Pt/SZ450 at 523 K for 5 h. Background spectra for (a) Pt/SZ300 and (b) Pt/SZ450 at 523 K are shown for reference.

523 K for 5 h (Figure 1c), characterized by the appearance of IR bands at 3652 and 3740 cm^{-1} assigned to the stretching vibrations of terminal and bridging isolated zirconium OH groups, respectively. Two additional broad bands at around 3050, and 3450 cm^{-1} were also observed, along with a band at 1612 cm^{-1}. For the inactive sample (Figure 1d), the spectrum only revealed the presence of isolated terminal and bridging OH groups (3740 and 3650 cm^{-1}) under the same conditions of H_2 adsorption: the bands at 3450, 3050, and 1612 cm^{-1} were no longer present. Therefore, the formation or absence of species corresponding to the 1612, 3050, and 3450 cm^{-1} bands due to H_2 adsorption is considered to be the critical factor determining the activity of Pt/SZ catalysts for H_2 adsorption.

The three bands at 1612, 3050, and 3450 cm^{-1} in Figure 1c can be gradually weakened by evacuation at 523 K. Ishikawa et al.[10] observed similar bands after H_2 adsorption onto Ru/ZrO_2, in which case these bands were assigned to H_2O-like species. Similar assignments can be implied for the present results. For confirmation, an H/D isotopic exchange experiment was performed, in which D_2 was introduced at 373 K and 400 Torr into the chamber holding the hydrogen-adsorbed Pt/SZ300 (spectrum shown in Figure 1c). Figure 2 shows the spectral changes over time during the isotopic exchange reaction. The three bands at 1612, 3050, and 3450 cm^{-1} weakened, and three new complementary bands slowly appeared at ca. 1418, 2400, and 2512 cm^{-1}. It can be seen that the terminal and bridging OH groups were gradually converted into their OD forms, which generate bands at 2768 and 2694 cm^{-1}. The vibrational frequency ratios of the last two bands are 1.270 and 1.373, respectively, while that of the first band prior to and following D_2 exchange is 1.137 (1612/1418). This exactly corresponds to the bending mode of H_2O-like species on Ru/ZrO_2 ($\delta_{H2O}/\delta_{HDO} = 1600/1400 = 1.137$),[10] confirming that these three bands are due to H_2O-related species in the Pt/SZ system. The band attributed to δ_{D_2O} was not identified because of poorly resolved spectra at ca. 1190 cm^{-1}.

The wide tailing of the OH stretching band of the presently observed water to low frequency ($\approx$2800 cm^{-1}) is distinguished from generally observed water adsorbed on oxides. This may be attributed to the presence of strong hydrogen-bonding interaction with SZ surface and also formation of water clusters.

The desorption behavior of the species formed by H_2 adsorption on Pt/SZ was examined through temperature-programmed desorption (TPD) measurements. Although the desorption peaks of H_2 from hydrogen-adsorbed Pt/SZ300 and Pt/SZ450 appeared at the same temperature (498 K), the H_2 desorption peak of Pt/SZ300 was appreciably weaker. In contrast, the H_2O desorption peak of hydrogen-adsorbed Pt/SZ300 was much stronger than that of Pt/SZ450. This suggests that the observed H_2O-related species formed by H_2 adsorption on Pt/SZ300 are largely desorbed as water. This differs from Ru/ZrO_2, for which the hydrogen atoms of the H_2O-like species desorbed as H_2 molecules when evacuated at higher temperature. Clear differences between the H_2O-like species formed on Ru/ZrO_2 by H_2 adsorption and the present adsorbed H_2O molecules can be seen by comparing the IR spectra. In the present study, adsorption of H_2 and H_2O onto Pt/SZ300 produced very similar species. Therefore, the three bands at 1612, 3050, and 3450 cm^{-1} are believed to be due to the formation of H_2O on Pt/SZ300 upon H_2 adsorption, resulting in the elimination of oxygen atoms from Pt/SZ300 during H_2 adsorption and desorption. In fact, the rate of H_2O formation from H_2 adsorption on Pt/SZ300 gradually decreased with repetition of the H_2 adsorption-desorption cycle.

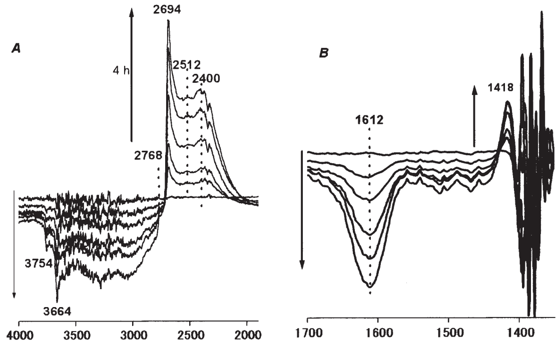

Figure 2. H/D isotopic exchange at 373 K on hydrogen-adsorbed Pt/SZ300 (Fig. 1c, gaseous H_2 was removed at room temperature by evacuation): A) OH stretching region, and B) HOH bending region.

The spectra of adsorbed hydrogen on active and inactive Pt/SZ catalysts (Figures 1c and d) reveal a clear difference between the two catalysts: water forms over Pt/SZ300 upon H_2 adsorption, while only isolated OH groups forms on Pt/SZ450. This is in good agreement with the TPD results, indicating that the active surface oxygen species responsible for the formation of H_2O upon interaction with H_2 are liberated by evacuation at 723 K as H_2O to form the inactive Pt/SZ450. These surface active oxygen sites may play an important role as active sites on Pt/SZ catalysts for alkane isomerization. This is supported by similar IR spectra for water observed for hydrated heteropoly acids, $H_3PW_{12}O_{40}\cdot nH_2O$ ($0 \leq n \leq 6$).[11]

In summary, active and inactive Pt/SZ catalysts were demonstrated to exhibit very different hydrogen adsorption behavior. H_2O and OH groups were formed on a Pt/SZ catalyst evacuated at 573 K upon H_2 adsorption, whereas only surface OH groups were formed on a similar catalyst evacuated at 723 K, direct evidence of the spillover of hydrogen from Pt to the support. However, the formation of a hydride intermediate was not observed directly.

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