

FTIR Spectra of Terminal and Bridged Hydrogen Atoms Adsorbed on Ruthenium Metal Particles Dispersed on Magnesium Oxide

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Infrared absorptions of adsorbed hydrogen atoms on 2 wt% Ru/MgO catalysts are observed at 1870, 1760 (both terminal species), and 1330 cm^{-1} (bridged species); this is the first observation of a bridged species on supported metal catalysts.

Ultra-high vacuum techniques and vibrational spectroscopy have never previously been used to observe terminal hydrogens adsorbed on a transition metal in a single crystal surface,¹ with the exception of hydrogen on a W(100) surface.² Two types of polycoordinated hydrogen atoms on Ru single crystal surfaces have been reported.¹

On the other hand, only terminal hydrogen atoms have been observed on supported metals by IR spectroscopy.³⁻⁵ The observed spectra can be assigned to terminally bonded hydrogen atoms (one being a twin or dihydrogen-like type) on the basis of recent results with metal single crystals.¹ On a doubly promoted iron catalyst, adsorbed hydrogen atoms give peaks in the 1900–1960 cm^{-1} region in Raman spectra.⁶ Thus, bridged hydrogen adsorbed on supported transition metals have not been observed previously. We have succeeded in obtaining IR spectra of both terminal and bridged adsorbed hydrogen atoms on Ru metal particles (Ru/MgO).

The study of hydrogen on Ru catalysts is very important, because of the importance of Ru catalysts in the Fischer-Tropsch synthesis, ammonia synthesis⁷ and hydrogenation of aromatics, such as, benzene.

A 2 wt% Ru/MgO sample was prepared by impregnating MgO with a tetrahydrofuran (THF) solution of $\text{Ru}_3(\text{CO})_{12}$ and then decomposing the carbonyls under vacuum at 673 K. The self-supported sample disk was mounted in a quartz IR cell. The sample was pretreated under 200 Torr (1 Torr = 133.322 Pa) of circulated hydrogen at 773 K for 12 h, and evacuated at the same temperature for 1 h. The Ru metal particles thus obtained had average diameters of 2.0 to 2.5 nm by TEM (transmission electron microscopy) measurements. Spectra were obtained with the integration of 32 to 64 scans, using an FTIR spectrometer with a triglycine sulfate detector (Japan Spectroscopic Co. Ltd.) having a resolution of 2 cm^{-1} .

The IR spectra of adsorbed hydrogen and deuterium on Ru/MgO are shown in Fig. 1. At 170 K, three peaks assigned to adsorbed hydrogen atoms were observed at 1870, 1760 and 1330 cm^{-1} , respectively [Fig. 1(a)]. These peaks were not sharp because of heterogeneity of adsorbed sites. The adsorbed species corresponding to the peak at 1870 cm^{-1} was desorbed at 170 K by evacuation, or by heating to room temperature even in the presence of gaseous hydrogen [Fig. 1(b)]. Thus, the species at 1760 cm^{-1} is adsorbed more strongly than the one at 1870 cm^{-1} . The two peaks at 1870 and 1760 cm^{-1} were reasonably shifted to 1350 and 1270 cm^{-1} by replacing hydrogen with deuterium [Fig. 1(d,e)]. Thus, the behaviour of these two bands were similar to the results from the Pt/ Al_2O_3 system reported by Pliskin and Eischens.³

In this work, a new band was observed at 1330 cm^{-1} [Fig. 1(a-c)]. This band was not observed at 350 to 400 K under vacuum. The new peak at 1330 cm^{-1} was assigned to an asymmetric stretching mode of bridged coordination by reviewing the hydride polynuclear complexes of various metals. Although it seems reasonable to assign this band to a species with twofold coordination,⁸ an electron energy loss (EELS) peak at 164 meV (1320 cm^{-1}) due to adsorbed hydrogen has been assigned to quasi-threefold hydrogen atom on a Ru(10 $\bar{1}$ 0) single crystal surface.¹ However, it was difficult to determine definitively whether or not the species have C_{2v} symmetry. Bridged hydrogen species should have two absorption modes of M-H stretching; asymmetric and symmetric.

The symmetric stretching is expected to occur at lower frequency than the asymmetric. However, in this work, it was not detected, probably because it occurred below 1000 cm^{-1} , the transpance limitation of this sample. A peak due to adsorbed deuterium corresponding to the hydrogen peak at 1330 cm^{-1} would be expected at ca. 950 cm^{-1} , however, it was not observed for the above reason.

The two bands at high frequency were thought to be due to an adsorbed hydrogen atom right on top of Ru, and hydrogen mostly on-top but interacted with neighbouring Ru atoms (or due to twin-type hydrogen atoms), respectively. If the latter is due to a twin-type, two stretching absorption modes (symmetric and asymmetric) should be observed. However, it was impossible to separate bands with small differences of frequency, probably less than 60 cm^{-1} as is seen in metal complexes.⁹ It is not reasonable to assign the peak at 1760 cm^{-1} to a bridged hydrogen atom bound to two Ru atoms, as was done in earlier discussions on Pt particles.^{3,10} Bridged

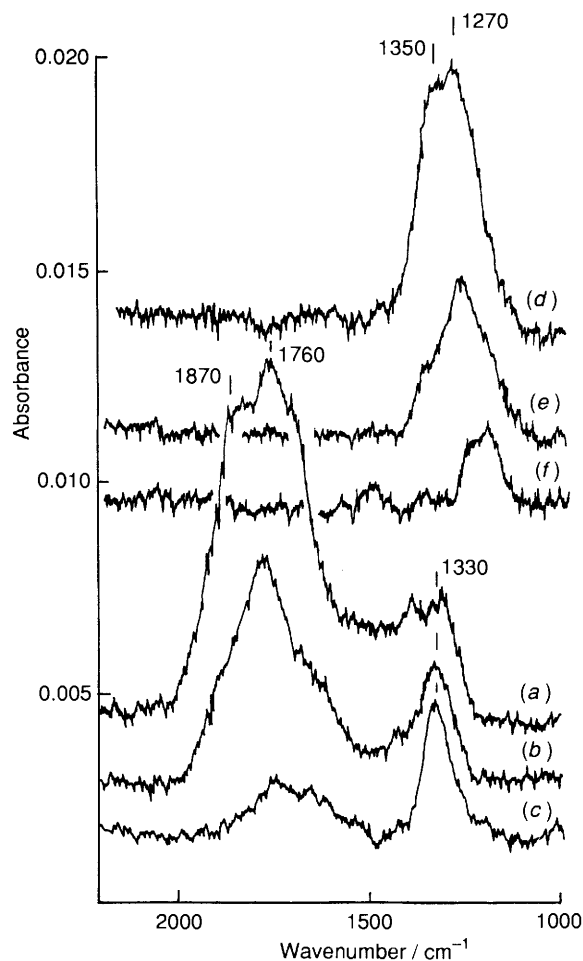


Fig. 1 FTIR spectra of adsorbed hydrogen and deuterium on 2 wt% Ru/MgO: under 50 Torr H_2 at 173 K (a), under 50 Torr H_2 at 300 K (b), then evacuated at 300 K (c), same as for (a), (b), and (c), using D_2 [(d), (e), and (f), respectively]

hydrogens on metal surfaces have been reported in the range 1500–1400 cm^{-1} by EELS also.

The IR spectra of dissociatively adsorbed hydrogen on Ru/MgO were observed for the first time at 1870, 1760 and 1330 cm^{-1} , the peaks were assigned to three kinds of adsorbates; two kinds of terminal species on a Ru atom and on a bridged species. The species at 1330 cm^{-1} is adsorbed most strongly, and this species was considered to be important under hydrogenation conditions. The bridged hydrogen atom was suggested for the first time on supported transition metal catalysts. On single crystal surfaces, terminal hydrogen atoms have not been reported probably due to their weak adsorption under vacuum.

IR studies of this kind are expected to clarify the role of adsorbed hydrogen in catalysis. For example, the presence of hydrogen has been reported to retard the dissociation of dinitrogen on Ru catalysts.¹¹ The role of hydrogen can be studied by IR methods, since adsorbed dinitrogen on Ru catalysts has recently been observed successfully by FTIR.¹²

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