

An Infrared Study of the Adsorption of CO on Supported Bimetallic Catalyst System

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Summary: Ruthenium-manganese bimetallic catalysts supported on alumina and silica were prepared by coimpregnation of high surface area alumina and silica with RuCl_3 and MnCl_2 . Infrared spectroscopy was used to investigate the adsorption of CO on the system. The study revealed that the presence of Mn not only produces a low frequency band but also results in the shift of IR bands. The data has been discussed in terms of ensemble and electronic effects and the change in surface geometry produced by the addition of Mn to the catalyst system.

Introduction

The possible preferential surface enrichment by one of the metallic components in either an alloy or a supported bimetallic clusters has attracted a great deal of attention over the last few years. With the development of modern sophisticated instrumentation, progress in this area has been very impressive [1]. The application of IR spectroscopy to the study of surfaces has brought major insight into the surface chemistry areas in which new information can be gained, which includes the structure of adsorbed species, the mode of interaction between the surface and the adsorbed species, surface structure and nature of the adsorption [2-16].

This study was conducted to investigate the effect of structurally modified surface due to addition of Mn on the stretching frequency of adsorbed CO.

Results and Discussion

Table 1 presents the IR frequency bands on the catalyst system on different supports. A new band appeared at 1755 cm^{-1} frequency, apart from this band two broad bands at 1860 and 1980 cm^{-1} frequency ap-

peared on the alumina and silica supported samples, another feature observed from the IR data is a shift in band at 1790 and 1800 cm^{-1} on the samples without Mn to lower frequency on the samples promoted with Mn, on the alumina and silica supports. This shift in band position is in agreement with the literature value [17], that alloying effects the position of IR bands. It is suggested here that one must consider the effect of electronic interaction between Ru and Mn on the system as one of the possibility of lower frequency shift. To justify a shift to lower frequency by electronic arguments, one would have to take into account that the second metal component acts as an electron donor, thereby increasing the electron density of Ru sites in close proximity to the donor atoms. Shifting of CO peak to lower frequencies could be caused by the back donation of electrons from d-orbitals of Ru to the antibonding $2\pi^*$ orbitals of CO. This argument is similar to what Schwank *et al.* [18] have observed on Pt-Au/SiO₂ catalyst. The difference in the stretching frequency in the bridge form between the silica and the alumina support is possibly due to the different metal dispersion on the two supports [19]. The broad band appeared at 2030 cm^{-1} frequency on

Table 1: IR bands observed after CO-chemisorption experiment on the catalyst system.

Catalyst sample	Wavenumber (cm ⁻¹)		FWHM
	Al ₂ O ₃ Supports	SiO ₂	
100:00	1640,1790,1860	1640,1800,1860	1860=0.25
	2030.	2030	1980=0.27
			2030=0.27
100:20	1640,1755,1787	1640,1755,1795	1860=0.31
	1860,1980,2030	1860,1980,2030	1980=0.33
			2030=0.37

100:00 and 100:20 samples on both the support is due to linearly bonded CO attached to the Ru metal. The broadening of linearly bonded CO on alumina and silica supported samples could be attributed to the elimination of particle size effect [20,21], the CO coverage [22] and due to presence of contamination which might be induced during sample preparation. It is known that the layer of hydrocarbon impurities on the surface could change the CO adsorption surface sites responsible for linearly bonded CO adsorption [23]. This broadening is more pronounced on Mn promoted samples. Hence it is proposed that the combination of geometric and electronic effect caused by the addition of Mn, might be one of the cause of this broadening [24].

Upon examining Table 1, it is also observed that the bands in the bridged form region actually consist of two bands located at 1860 and 1787-1795 cm⁻¹, apart from a new band which appeared at 1980 cm⁻¹ on the Mn promoted samples. It is suggested here that in coordination chemistry it has been shown that a degree of back donation increases with the number of metal atoms involved in bond formation with CO molecules i.e., for two centered bonded CO they vary between 1750 to 1880 cm⁻¹ [25,26]. It might be indicative of the existence of a non negligible portion of CO molecules bonded to three metal atoms, in addition to the CO molecules "bridging" two Ru atoms. It is note worthy that the species bonded to more than two metal atoms prevails at low coverage [27]. The appearance of band at 1980 cm⁻¹ on the Mn enriched samples is possibly due to formation of RuMn mixed sites, which we have observed in TEM, SSIMS, XRD experiments [28]. The band at 1640 cm⁻¹, which was observed on silica and alumina supports and on the samples with and without Mn, can be attributed to the presence of hydrocarbon contaminations. Fukushima *et al.*, [29] observed a band at 1520 cm⁻¹ on Rh-Mn/SiO₂ catalyst system. They reported that this extraordinary shift on the system is

due to the presence of Mn²⁺ on the surface. On the other hand Shriver *et al.* [30], have proposed a bifunctional activation of bridged CO in the adducts of carbonyl metal clusters with Lewis acid reagents such as AlBr₃ and BF₃. They exhibit a large reduction of IR frequencies from 1640 and 1820 cm⁻¹ in clusters to 1390 and 1548 cm⁻¹ in the adduct complexes respectively. A distinct characteristic of metal carbonyls bridging to the Lewis acid and a small increase for ν_{CO} for all remaining linear carbonyls, affording good evidence for adduct formation at the bridging carbonyl oxygen. Knozinger *et al.* [31], also observed a low frequency band at 1715 cm⁻¹ on Mn promoted Rh/Silica system, and they thought that this is due to a tilted Rh-C-O-Mn species. On the basis of the argument presented above, it is proposed that the discrepancy which exists between this system and the Mn promoted system discussed in the literature is due to:

- (i) the different precursor used in catalyst preparation.
- (ii) due to the formation of MnO rather than Mn₂O₃ or other oxide on the surface.

Experimental

The catalyst samples supported on alumina and silica support were prepared by the procedures described in reference [28]. The catalyst samples to be studied were pressed into disk and CO-chemisorption experiment was carried out in a separate experimental set up. The disk was then placed in an IR cell. The IR spectra was recorded at room temperature using a research grade FTIR (Digilab FTS 40) instrument.

Conclusions

From the IR studies one can derive the following conclusions;

- (i) the presence of Mn produces a low frequency band and effects the CO stretching frequency electronically and geometrically.
- (ii) the presence MnO and Mn_xO_x species on the surface effects the IR bands.
- (iii) the broadening of linearly bonded CO band is caused typically due to the changes induced on the surface of the system.
- (iv) process of alloying lower the IR frequency.

- (v) the presence of modified surface due to presence of Mn was confirmed due to appearance of IR bands on the Mn doped samples.

References

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