JOURNAL OF CATALYSIS **16**, 189-196 (1970)

Surface Species on Manganese

GEORGE BLYHOLDER AND MARVIN C. ALLEN*

Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701

Received June 2, 1969; revised July 3, 1969

Infrared spectra of the stable surface species formed at 25°C by the interaction with a Mn surface of methanol, ethanol, *n*-propanol, *n*-butanol, isobutanol, 2-propanol, 2-butanol, *t*-butanol, diethyl ether, tetrahydrofuran, acetaldehyde, acetone, allyl alcohol, and methyl vinyl ether have been obtained. From the spectra it is concluded that: (i) alkoxides are quite stable surface species, (ii) a coordinate covalent bond of oxygen to the surface is not stable, (iii) the O-H bond is readily broken, (iv) the degree of surface coverage by alkoxide structures is in the order primary > secondary > tertiary, (v) the C=C bond does not strongly add to the surface, and (vi) the C-H bond does not readily break at 25°C to form dissociatively adsorbed hydrocarbons. It is suggested that attachment of a reacting complex to the Mn surface is more likely to be through an oxygen atom than a carbon atom.

INTRODUCTION

A fundamental understanding of catalysis requires a knowledge of the detailed nature of surface species. For example, in the dehydration and dehydrogenation of alcohols on metals both metal-carbon and metal-oxygen bonds have been proposed as the main mode of attachment of the alcohol to the surface (*1*). While no complete catalytic reactions are dealt with here, the structures of a number of surface species formed on manganese are determined by infrared spectroscopy. Manganese is a widely used catalyst constituent. On metallic manganese it is shown below that metal-oxygen bonds form far more readily than do metal-carbon bonds. It should be recognized that we are here determining the stable surface species at 25°C. These are not reaction intermediates in our system and are not necessarily the structures of reaction intermediates under different conditions. However, we believe that reaction intermediates proposed on the basis of a knowledge of stable surface species are much more likely to be meaningful than intermediates proposed in the absence of such knowledge.

When it can be obtained, infrared spectral data has proved to be one of the most effective means of obtaining structural information about adsorbed species. The only previous infrared work dealing with species adsorbed on Mn concerns chemisorbed CO (*2*). In the present study, the infrared spectra of a variety of alcohols, aldehydes, ketones, and ethers, both saturated and unsaturated, adsorbed on Mn were examined.

EXPERIMENTAL METHOD

The wide spectral range experimental technique, which has been described in detail elsewhere (*3*), consists of evaporating Mn from an electrically heated tungsten filament in the presence of a small pressure of helium. The metal particles formed in the gas-phase deposit in a hydrocarbon oil film on the salt windows of an infrared cell. The gas to be studied is then admitted to the cell, and the spectrum of the chemisorbed species obtained. Spectra are recorded before and after admission of the gas to the cell. Five min of pumping has been found sufficient to remove all spectra due to gas-phase molecules. For three and four carbon atom molecules, 30 min of pumping may be re-

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* Present address: Continental Oil Co., Ponca City, Oklahoma.

quired to remove molecules dissolved in the oil film. The 25°C temperature listed for measurements is an average as all measurements were taken at room temperature.

The spectra were obtained using Perkin-Elmer models 21 and 337 spectrophotometers. The model 21 is equipped with CsBr optics which permit scanning from 715 to 250 cm^{-1}. The 337, which is a grating instrument, is used to scan the region from 4000 to 400 cm^{-1}. No unusual spectrometer settings were used.

The adsorbates were obtained as reagent grade chemicals from commercial sources. They were degassed by repeated freeze–thaw cycles in the vacuum system. The CO was passed through an activated charcoal trap cooled with liquid air.

This technique has the advantage that a wide infrared spectral region is available for study. It has the disadvantage that the metal surface is covered with oil. This oil is apparently only weakly adsorbed since many gases have been found to chemisorb readily on the metal. Essentially, the oil is regarded as a solvent which has weak interactions with the systems of interest. Having a wide spectral range available aids greatly in attempts to determine structure.

SPECTRA AND INTERPRETATION

The spectral bands for primary alcohols chemisorbed on Mn at 25°C are listed in Table 1. The primary alcohols studied are methanol, ethanol, *n*-propanol, *n*-butanol, and *i*-butanol. A typical spectrum, that for *n*-propanol, is shown in Fig. 1. All of the spectra are for the stable surface species at 25°C which remain after the cell has been evacuated for more than 0.5 hr.

In all cases the assignments in Table 1 lead to principal stable surface species which have an alkoxide structure. The assignments have been made by comparison with the spectra of alcohols. In some cases detailed assignments were not available in the literature, but even here the spectrum of the adsorbed species is in good agreement with that of the alcohol. In fact, the agreement in all cases is so good that one may wonder why substituting a metal atom for an H atom does not have a larger effect on skeletal vibrations. This agreement is due to both the H and the metal having little effect on the skeletal vibrations. The H atoms have little effect because, while the O–H force constant is large, hydrogen is too light to greatly affect skeletal vibrations. In the case of metal

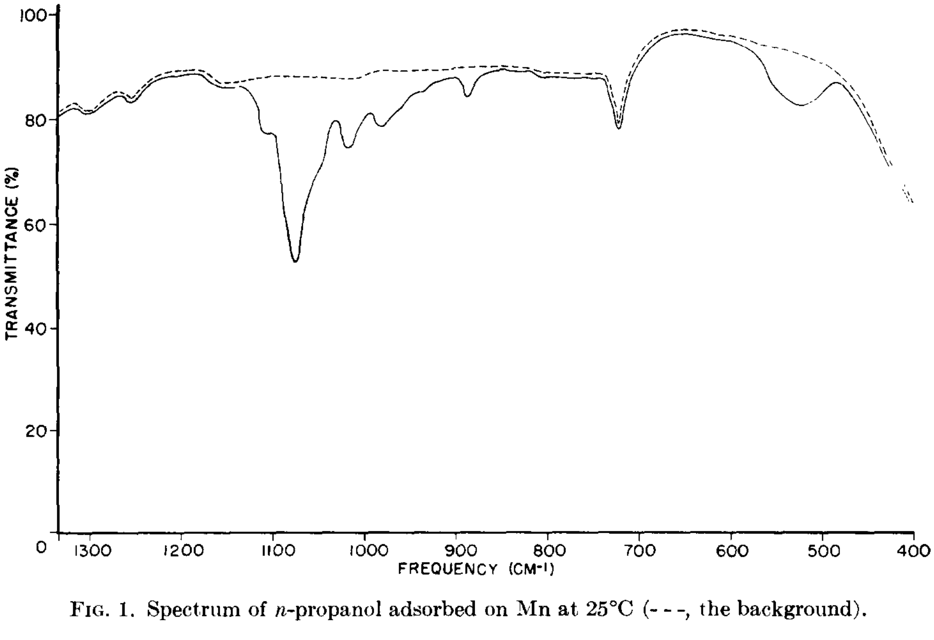

FIG. 1. Spectrum of *n*-propanol adsorbed on Mn at 25°C (- - -, the background).

TABLE 1
INFRARED SPECTRA OF PRIMARY ALCOHOLS ADSORBED ON MANGANESE AT 25°C

Methanol on Mn	Liquid methanol[a]	Ethanol on Mn	Liquid ethanol[a]	*n*-Propanol on Mn	Liquid *n*-propanol[b]	*n*-Butanol on Mn	Liquid *n*-butanol[c]	*i*-Butanol on Mn	Liquid *i*-butanol[d]	Assignments[a]
2810 sh	2820 s									O–CH_3 str.
			1273 m							CH_2 twist
			1149 w		1140 w	1118 w	1114 m		1140 w	CH_3 rock
1075 m	1112 s	1105 m	1089 s	1108 m	1100 m	1074 m	1070 vs		1118 m	CH_3 rock
1050 m							1057 sh			
1035 sh	1030 s	1058 m	1050 s	1075 m	1075-1060 s	1050 sh	1043 s	1055 m	1048 sh	Skeletal str.
				1018 m	1020 s			1020 sh	1032 s	CH_2 rock
				972 m	990 m	996 w	997 m	955 w	967 m	CH_3 rock
					972 w	965 w	954 m			
					918 w			930 vw	942 m	CH_3 rock
					908 w	900 w	905 w		908 m	
		888 w	880 s	888 m	890 w	850 w	853 m			Skeletal str.
					860 w				878 m	
			802 w			785 vw	799 vw		821 w	
		540 w		540 m		540 m		550 w		M–O str.
	470 w		433 m		460 w		460 w		480 m	Skeletal bend

[a] Tanaka, C., *Nippon Kagaku Zasshi* **83,** 792 (1962).

[b] Am. Petrol. Inst. Proj. 44, Spectrum No. 427; [c] No. 429; and [d] No. 430.

atoms the metal–oxygen bond is relatively weak so that the metal–oxygen frequencies are expected to be around 400–500 cm^{-1}. It is a well-known principle that, where there is a large separation in force constant or vibrational frequencies, the modes of motion are fairly independent (*4*). This agreement between alkoxide spectra and free alcohol spectra has also been found in the few infrared spectra that have been reported for Al and Ti alkoxides (*5–8*).

In the case of methanol adsorption an alkoxide structure is further supported by the presence of the band at 2810 cm^{-1} because a band in this region is indicative of a methyl group attached to an oxygen atom (*9*). In all but one of these spectra a medium to weak intensity band occurs near 540 cm^{-1}. There are no alcohol skeletal vibrations within 60 cm^{-1} of this band. The one new feature expected in these spectra would be a band due primarily to a metal–oxygen stretching mode, which band would be expected to be in this region (*8*). Therefore, the band near 540 cm^{-1} in each spectrum has been tentatively assigned to the metal–oxygen stretch.

The possibilities of some other structures were considered and discarded for a variety of reasons. Structures containing hydrogen atoms attached to unsaturated carbon atoms were eliminated because of the absence of C–H stretching vibrations above 3000 cm^{-1}. While the oil blocks out the saturated C–H stretching region, bands for unsaturated C–H groups which usually occur near 3100 cm^{-1} should be clearly visible. Structures containing O–H groups were eliminated because of the absence of O–H stretching and bending vibrations which are clearly evident when gas phase alcohol is in the cell. The intensity of OH bands for free alcohols is near that of the other bands so that, if the surface structures contain OH groups, their bands should have been observable. Likewise, structures containing carbon–oxygen double bonds were eliminated because of the absence of a band around 1700 cm^{-1}. Even π-complexed double bonds are only shifted within about 100 cm^{-1} so these too are presumed absent. Two-point (or more) attachment to the surface, in which both a carbon–metal and an oxygen–metal bond are present, is eliminated in the case of methyl alcohol adsorption because of the presence of the CH_3 rocking band at 1060 cm^{-1} and in the other cases because multiple attachment is expected to perturb the skeletal vibrations more than is observed. It should be noted that the skeletal vibrations of different chain length alcohols and the alkyl group of an alcohol are all distinctly different; e.g., the skeletal vibrations of CH_3CH_2–, CH_3CH_2O–, $CH_3CH_2CH_2$–, and $CH_3CH_2CH_2O$– are all distinctly different. We also

TABLE 2

INFRARED SPECTRA OF SECONDARY AND TERTIARY ALCOHOLS ADSORBED ON MANGANESE AT 25°C

2-Propanol	Liquid propanol[a]	2-Butanol on Mn	Liquid 2-butanol[b]	*t*-Butanol on Mn	Liquid *t*-butanol[c]	Assignments[a,d]
	1250 s					OH bend
1155 m	1162 s	1160 w	1150 m	1230 w	1242 m	Skeletal str.
1132 m	1130 sh	1130 sh	1135 sh	1185 m	1201-1185 s	Skeletal str.
	1113 vw	1112 m	1112 s			CH_3 rock
		1032 m	1030 s		1023 m	CH_3 rock
970 m	950 s	992 m	990 s			CH_3 rock
		918 m	912 s	935 m	915 s	Skeletal str. + CH_3 rock
	818 w	820 w	820 m	765 w	750 m	Skeletal str.
550 vw		555 m		550 m		M–O str.
	485 m		490 vw	470 w	465 m	Skeletal bend
	420 m					Skeletal bend

[a] Tanaka, C., *Nippon Kagaku Zasshi* **83,** 521, 657 (1962).

[b] Am. Petrol. Inst. Proj. 44, Spectrum No. 431; and [c] No. 432.

[d] Tanaka, C., *Nippon Kagaku Zasshi* **83,** 398 (1962).

then expect M–CH_2–CH_2–O–M, where M is a surface metal atom, to have distinctly different skeletal vibrations. The close agreement between alcohol skeletal frequencies and the observed spectra for surface species in all cases studied, which includes quite a diverse range, leads us to suggest that on our surfaces the attachment to the surface is via the oxygen atom and not the carbon atom, that attachment by more than one atom per molecule does not occur, and that the spectra represented mostly a single surface species and not a mixture. When it is stated that other structures are eliminated, it is not meant that they cannot exist in small concentrations on the surface but only that they do not exist in sufficient concentration to be observed in our spectra.

The spectral bands for the secondary alcohols, 2-propanol and 2-butanol together with the tertiary alcohol, *t*-butanol, are listed in Table 2. As in the case of the primary alcohols, the correspondence of the spectra of the adsorbed species to the liquid alcohols leads to the conclusion that an alkoxide structure predominates on the surface for the secondary and tertiary alcohols. The intensity of the spectra suggests that less secondary than primary alcohol is adsorbed on the surface and that still less tertiary alcohol is adsorbed. This is presumed to be due to steric factors.

The ethers, diethyl ether and tetrahydrofuran, gave no infrared evidence of adsorbing. The Mn samples chemisorbed CO in a normal manner after exposure to the ethers, thereby showing that the surfaces had not become contaminated. These experiments are taken as indicating that the often proposed mode of a gas adsorbing by a lone pair of electrons on an oxygen atom coordinating with a surface metal atom is not a strong enough interaction to produce stable surface species at room temperature.

The behavior of an aldehyde, acetaldehyde, was investigated and the results are shown in Table 3. The most intense bands correspond closely to those produced by adsorption of ethanol, which has been concluded to be an alkoxide structure. These bands at 1092, 1060, and 550 cm^{-1} are quite far removed from any bands for liquid acetaldehyde. Again the band at 550 is tentatively ascribed to the metal–oxygen bond holding the complex to the surface. The weak band at 1740 cm^{-1} is presumed to be due to an acyl structure on the surface. Since the C=O stretch normally produces a very intense band and the 1740 band is very weak, there seems to be relatively little acyl structure on the surface. In order to form an alkoxide structure from an aldehyde a hydrogen atom must be added. The hydrogen can come from either some of the oil matrix or some of the acetaldehyde cracking on the metal surface. The fact that a surface alkoxide structure forms from the adsorption of an aldehyde is taken as an indication of the stability of an alkoxide structure on the surface.

The results of adsorbing a ketone, acetone, is also given in Table 3. The bands for the adsorbed species are shown in Table 3 to correspond closely to the bands from adsorbed 2-propanol which forms an alkoxide structure. The isopropoxide surface structure can form from acetone by the addition of a hydrogen atom without any rearrangement of the carbon–oxygen skeleton. As before this extra hydrogen can come from either cracking of the oil matrix or some of the acetone on the Mn surface. The weakness of the bands suggests that the number of recognizable surface species is relatively small. Again the stability of the surface alkoxide structure is demonstrated.

Because of the interest in the behavior of unsaturated compounds on metal surfaces, the adsorption of allyl alcohol was investigated. The infrared bands for the surface species formed and for liquid allyl alcohol are listed in Table 4. The close correspondence of these two spectra strongly suggests the formation of an alkoxide surface species with the carbon–oxygen skeletal chain from allyl alcohol unchanged. While it has often been suggested that a carbon–carbon double bond may readily interact with a metal surface by either associative adsorption or π-complexing, we see in this case on Mn the competition between the double bond and the

TABLE 3

INFRARED SPECTRA OF ALDEHYDES AND KETONES ADSORBED ON MANGANESE AT 25°C

Acetaldehyde on Mn	Ethanol on Mn	Liquid acetaldehyde[a]	Assignments[a]	Acetone on Mn	2-Propanol on Mn	Liquid acetone[b,c]	Assignments[b,c]
1740 vw		1745 vs	Acyl CO str.			1725 vs	CO str.
						1221 m	CH_3 rock
		1258 m	CH_3 rock + C–H def.	1150 w	1155 m		CH_3 rock + skel. str.
		1241 m	CH_3 rock + C–H def.	1120 w	1132 m	1100	C–C–C asym. str.
1092 w	1105 m		CH_3 rock	970 w	970 m	990 m	
1060 vw	1058 m		Skeletal str.			885 m	
		917 w	Sym C–C str.			781 w	
		890 w	CH_3 rock	550 w	550 w		M–O str.
550 vw	540 w		M–O str.				

[a] Tanaka, C., *Nippon Kagaku Zasshi* **83,** 398 (1962).

[b] Corin, C., *J. Chem. Phys.* **32,** 241 (1935).

[c] Cossee, P., Schachtschneider, J. H., *J. Chem. Phys.* **44,** 97 (1966).

TABLE 4
Infrared Spectra of Unsaturated Compounds Adsorbed on Manganese at 25°C

Allyl alcohol on Mn	Liquid allyl alcohol[a]	Assignments[a]	Methyl vinyl ether on Mn	Methanol on Mn	Assignments
3017 vw	3105 m	CH_2=	2815 sh	2810 sh	O–CH_3 str.
1640 vvw	1650 m	C=C str.	1060 m	1075 m	CH_3 rock
	1830 w	Overtone	1040 sh	1050 m	CH_3 rock
1420 sh-vw	1420 m	CH_2 def.	1030 m	1035 sh	C–O str.
1350 sh-vw	1350 m	CH def.			
1110 w	1105 s	=CH_2 rock			
1062 m	1030 vs	CO str.			
992 w	995 vs	CH def.			
912 m	920 vs	CH_2 def.			
885 w	880 w	Skeletal str.			
620 vvw	640 w				
550 vw	550 m	Skeletal bend			
465 vw		M–O str.			

[a] Nakanishi, K., "Infrared Absorption Spectroscopy." Holden-Day, San Francisco, 1962.

alcohol group to interact with the surface results in interaction of the alcohol function. Again the stability of the alkoxide structure is demonstrated.

To further define the behavior of unsaturated compounds, the infrared spectrum resulting from exposure of the manganese surface to methyl vinyl ether was obtained. Having previously determined that ethers do not produce stable surface species, if methyl vinyl ether is to interact with the surface, it must do so through the double bond. The spectrum in Table 4 indicates only a small fraction of the surface is covered. The weak bands formed correlate well with a methoxide surface species as shown in Table 4. Apparently, the double bond provides enough of an interaction with the surface to allow time for some dissociation to occur.

Discussion and Conclusions

While there have been few previous structural studies of oxygen-containing molecules adsorbed on Mn, there have been several infrared studies of oxygen-containing molecules adsorbed on other substrates. Adsorption of alcohols on the oxides, silica, alumina, and magnesia near room temperature produces largely physically adsorbed alcohols and an alkoxide structure (*10–12*). At higher temperatures reactions occur to further alkylate the surface and produce carboxylic acids on the surface (*10–13*). Aldehydes and ketones give physically adsorbed molecules at room temperature on silica with the aldehyde producing some condensation products at 120°C (*14*).

On metallic surfaces the results are more varied, depending on the metal. The adsorption of oxygen containing molecules on Mn reported here closely parallels results previously reported for adsorption on Fe (*15*). However, these results are in strong contrast to results for Ni. On Ni, primary alcohols and acetaldehyde decompose at room temperature to produce chemisorbed CO while secondary and tertiary alcohols, ketones, and ethers do not produce stable surface species detectable by our infrared technique (*16*). Using silica supported Ni, Young and Sheppard (*17*) likewise found no acetone adsorption at 25°C and some decomposition of acetaldehyde to chemisorbed CO but, interestingly, much less acetaldehyde decomposition on their silica supported Ni than we have found on oil supported Ni. At 200°C acetone is found to crack in the presence of H_2 on silica supported Ni (*17*).

The behavior of the alcohols, aldehyde, ketone, ethers, and unsaturated compounds detailed above leads to the following conclusions concerning a manganese surface: (i) A coordinate covalent bond of oxygen to the surface is not stable. (ii) The O–H bond is readily broken. (iii) Alkoxides are quite stable surface species. (iv) The degree of surface coverage by alkoxide structures is in the order primary > secondary > tertiary. (v) The C=C bond does not strongly add to the surface. (vi) The C–H bond does not readily break at room temperature to form dissociatively adsorbed hydrocarbons.

This behavior pattern suggests that in the catalytic interaction of alcohols, aldehydes, or ketones with manganese surfaces, attachment of the reacting complex to the surface is more likely to be through an oxygen atom than a carbon atom.

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