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NOTES

Infrared Studies of Adsorption of Acetone on MgO and NiO

A number of catalytic reactions in which ketone is one of the products or of the reactants are known to proceed on oxide catalysts. However, the mechanism of the adsorption of ketone is still unclear. There seems to have been very few studies (*1*, *2*) of infrared spectra of ketone adsorbed on oxides. In the present work by using infrared technique the nature of the surface species formed by chemisorption of acetone on MgO and NiO and also the thermal stability of these species have been investigated.

Magnesium oxide was prepared by burning magnesium metal ribbon, as described by Kagel and Greenler (*3*). Nickel hydroxide was prepared from nickel nitrate. These oxide and hydroxide were pressed into a circular disk of 20 mm diameter. The disk was degassed for 1 hr at 100°C and then the temperature was slowly increased to 500°C and degassing was continued for 2 hr. Surface areas of MgO and NiO were 10.9 and 14.4 m^2/g, respectively. The adsorption of acetone was carried out at 5 mm Hg. The ir cell similar to that of Peri (*4*) was used.

A summary of the bands of adsorbed acetone and their assignments is shown in Table 1.

Figure 1 shows the typical spectra of acetone and acetone-d_6 adsorbed on magnesia at 25°C. The spectra in the 4000–2000 cm^{-1} region were not observed because of high scattering by the magnesia powder. The spectra changed gradually with time of adsorption, especially in the region 1700–1600 cm^{-1}. In this region, continuation of adsorption for 20 hr led to the appearance of both bands at 1700 and 1550 cm^{-1}, the latter being initially absent. Similar behavior is observed with acetone-d_6 adsorbed on MgO.

The spectra obtained with undeuterated acetone on NiO also changed with time of adsorption. After adsorption for 20 hr, instead of the band at 1700 cm^{-1} for MgO, the band at 1608 cm^{-1} having a shoulder band near 1558 cm^{-1} appeared.

As regards the bands at 1462 and 1364 cm^{-1} (Fig. 1), the corresponding bands are observed at 1096 and 1056 cm^{-1} with deuterated acetone. From the observed shift on deuteration, it is concluded that these bands are due to the asymmetric and symmetric bending vibrations of CH_3 group (*5*). The band at 1250 cm^{-1} (Fig. 1c) may be assigned to the carbon framework stretching vibration since the corresponding band of gaseous acetone appears at 1224 cm^{-1} (*5*). The assignment of the band at 1306 cm^{-1} observed with acetone-d_6 is unclear.

The bands around 1700–1500 cm^{-1} observed on MgO and NiO show a small shift in frequency on deuteration. This suggests that these bands are due to the vibrations associated with carbon–carbon and carbon–oxygen linkages. For the interpretation of these bands, the spectra of acetone-d_3 adsorbed on NiO were investigated where the spectra in the region above 2000 cm^{-1} were obtained because of its high transmittance. As shown in Fig. 2, two sharp bands at 2710 and 2210 cm^{-1} and a broad band centering around 2600 cm^{-1} appeared. From comparison of curves 2b and d, the sharp bands can be attributed to the OD and CD stretching vibrations, respectively. It seems that the broad band is due to pur-

TABLE 1
INFRARED BANDS OF ACETONE ADSORBED AT 25°C (cm^{-1})

Acetone on MgO		Acetone-d_6 on MgO		Acetone on NiO		Acetone-d_6 on NiO		
A[a]	B[a]	A[a]	B[a]	A[a]	B[a]	A[a]	C[a]	Vibrational mode
						2710		OD stretch
							2600	Hydrogen bonded OD stretch
						2210	2210	CD stretch
1700	1700	1688	1688					C=O stretch
1650								Unassigned
1610			1604			1610		
		1580						
				1608	1608	1580	1580	C=O stretch
1560	1550	1550	1550		1558	1540	1540	$C\overset{-}{\cdots}O$ stretch
1462	1462			1436	1462			CH_3 asym bend
1364	1364			1378	1378			CH_3 sym bend
		1328				1324	1324	Enolate complex?
		1306	1306	1310				Unassigned
1254	1250			1224	1224			Carbon framework stretch
		1096	1096			1095	1095	CD_3 asym bend
		1056	1056			1052	1052	CD_3 sym bend

[a] Time of adsorption: A, 5 min; B, 20 hr; C, 90 min.

turbed OD groups. Such behavior suggests that a dissociative adsorption of acetone takes place, the hydrogen removed being attached to the oxide ion. A referee suggested the possibility that the OD groups originate from the exchange reaction of D atoms of acetone-d_6 with surface OH groups. However, such possibility might be eliminated, since before the adsorption of acetone-d_6 the catalyst was treated with D_2O vapor at 450°C followed by evacuation at the same temperature, leading to the surface containing no OH groups.

As shown in Fig. 2, there is parallel increase in the intensities of the bands at 2600 and 1540 cm^{-1}. This suggests that the band at 1540 cm^{-1} results from a surface species formed by a dissociative adsorption of acetone. The band at 1324 cm^{-1} may be attributed to the same surface species, but the details are unclear. The intensity of the band at 1540 cm^{-1} increases with decreasing intensity of the band at 1580 cm^{-1}, indicating that the surface species associated with the former band is formed from that associated with the latter band. The fact that in the case of MgO the band around 1550 cm^{-1} was initially absent and appeared after adsorption for 20 hr would be expected from such behavior with NiO as just described above. Thus, it can be concluded that the band at 1540 (acetone-d_6–NiO), 1558 (acetone–NiO) and 1550 cm^{-1} (acetone–MgO and acetone-d_6–MgO) are assigned to the dissociatively adsorbed acetone, i.e., the enolate complex ($CH_2\overset{-}{\cdots}C(CH_3)\overset{-}{\cdots}O$) (*1*, *6*) and the bands at 1580 (acetone-d_6–NiO), 1608 (acetone–NiO), 1688 (acetone-d_6–MgO) and 1700 cm^{-1} (acetone–MgO) to the coordinately adsorbed acetone.

It is well known that acetone forms a strong coordination complex with Lewis acids such as aluminum and boron halides leading to a marked shift of the carbonyl band to a lower frequency (*7*, *8*). For acetone adsorbed on silica gel a shift of 92 cm^{-1} was found by McManus, Harano and Low (*9*). Similar shift would be expected for the carbonyl groups coordinated with the surface of oxides such as MgO and NiO, thus confirming the above conclusion. The carbonyl band is observed at 1608 cm^{-1} on NiO and at 1700 cm^{-1} on MgO,

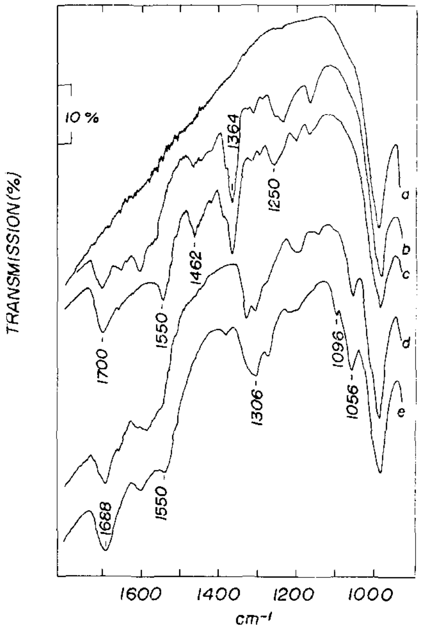

FIG. 1. Spectra of acetone and acetone-d_6 on MgO. (a) MgO (115 mg) outgassed at 500°C; (b) after 5 min adsorption of acetone and 2 min evacuation at 25°C; (c) after 20 hr adsorption of acetone followed by 1 hr evacuation at 25°C; (d) after 5 min adsorption of acetone-d_6 and 2 min evacuation at 25°C; (e) after 20 hr adsorption of acetone-d_6 followed by 30 min evacuation at 25°C. (In Figs. 1 and 2, the ordinates are displaced to avoid overlapping of traces.)

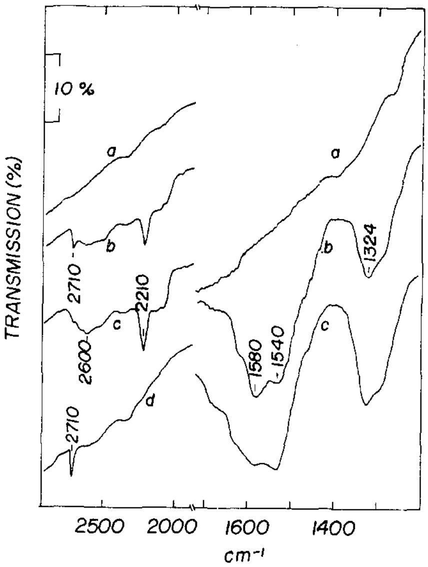

FIG. 2. Spectra of acetone-d_6 adsorbed on NiO. (a) NiO (135 mg) outgassed at 450°C; (b) after 5 min adsorption of acetone-d_6 and 2 min evacuation at 25°C; (c) after 90 min adsorption of acetone-d_6 and 2 min evacuation at 25°C; (d) after 30 min adsorption of D_2 at 90°C.

the frequency of the former being 92 cm^{-1} lower than that of the latter, i.e., acetone is adsorbed much more strongly by coordination on NiO than on MgO. As shown in Figs. 1 and 2, the enolate complex of acetone-d_6 is formed after adsorption for 5 min on NiO and after 20 hr on MgO. This suggests that formation of the complex takes place much more easily on NiO than on MgO.

The spectra of acetone adsorbed on the oxides changed with increasing evacuation temperature. On raising the temperature of the MgO disk containing acetone-d_6 up to 250°C, the bands due to coordination and enolate complexes disappeared, and new bands appeared at 1572 and 1406 cm^{-1}. Similar results were obtained on NiO, where a pair of the bands at 1556 and 1395 cm^{-1} appeared at 150°C. It has been reported by various workers that in the adsorption of acetone (*1*, *2*) as well as of alcohol (*2*, *10–13*) on metal oxides at high temperature the carboxylate ions are formed, a pair of the bands being observed 1570–1550 cm^{-1} and 1470–1400 cm^{-1}. This suggests that the bands obtained after increasing temperature can be assigned to the asymmetric and symmetric O–C–O stretching vibrations.

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