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State of Pd in Active Methanol Synthesis Catalysts

H. DELIGIANNI,[1] R. L. MIEVILLE, AND J. B. PERI

Amoco Oil Company, Amoco Research Center, P.O. Box 400, Naperville, Illinois 60566

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An attempt was made to relate specific types of CO adsorption sites as characterized by IR with the methanol synthesis activity of several Pd catalysts supported on silica and Li-promoted silica. With unpromoted silica, the mode of addition of Pd, whether impregnated or ion-exchanged into the surface, had little effect on subsequent activity. Similarly, the Pd concentration did not play a major role in determining activity. However, IR spectra showed that different preparation procedures made significant differences in the way CO was held on the Pd. Li promoted the activity of Pd, in some cases by a factor of 6, with only minor changes in CO spectra. Changes seen in the spectra of CO held on Pd when Li was present did, however, show alterations in bridged bonding of CO held on Pd, reflecting either an electronic effect or changes in the face exposure of the Pd crystallites. Differences observed in the state of dispersion of the Pd evidently contribute little to synthesis activity. No IR evidence was seen for ionic sites or other effects of Li on the oxidation state of Pd, as shown by linear CO bands above 2000 cm^{-1}. Changes in bridged bonding of CO caused by Li might explain increased activity of methanol synthesis, but little evidence was seen for a general correlation of specific adsorption of CO with activity.

INTRODUCTION

It is generally agreed that there are at least two main requirements for an active methanol synthesis catalyst (*1–4*). First, the catalyst should adsorb CO without dissociating the molecule. Second, the catalyst should adsorb H_2 dissociatively (*5*). The first requirement of nondissociative CO adsorption is thought to be the more critical and complex of these catalyst properties. While nondissociation of CO is desired, the CO should also be "activated" sufficiently that H_2 can be attached to both ends of the molecule. These CO adsorption properties are generally provided by metals having atomic configurations with nearly or totally filled *d*-shells (*6*). For the current most active catalyst, this property is provided by Cu; other active metals, such as Rh, Pd, and Pt, fall within this category (*2, 7*). The oxidation states of these metals should strongly influence their "*d*" character and, therefore, their reactivity. In the case of Cu, the active oxidation state is not known. Although Cu^{1+} has been suggested (*6*), Cu^0 is the only observable species present under reaction conditions (*8*).

Pd/SiO_2 catalysts with and without promoters for methanol synthesis have been previously studied (*9–13*), with partially contradictory conclusions. Lunsford *et al.* (*10*) concluded that Pd structural effects play an important role in the activity of the catalyst, since catalysts with small Pd crystallites produce methanol while larger crystallites produce methane. Such structural effects can be induced by different grades of silica support. On the other hand, Ponec *et al.* (*9, 13*) believe that electronic factors are more important and ionic Pd sites are the centers for CO activation. The number of such sites is presumably increased by the presence of alkali metals. The effect of alkali metals such as Li appears to be more complex (*12*). Whatever the nature of the active centers, the addition of basic metals as well as the use of basic supports (*11*) promotes reactivity.

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[1] Present address: Chemical Engineering Department, University of Illinois, Urbana, Ill. 61801.

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TABLE 1

Metal Concentration (ppm)[a]

Silica	Na	Ca	Mg	Ba
Davison 57	355	982	209	13
Davison 59	396	530	137	5

[a] As measured by inductively coupled plasma.

Influence of the support can induce partial oxidation of supported metals, resulting in a frequency shift of the infrared bands arising from adsorbed CO. The purpose of the present study was to determine if a relationship could be observed between the IR bands of CO adsorbed on Pd and the performance of the catalyst. The choice of Pd/SiO_2 over a Cu catalyst system was based on practical considerations, despite the lower activity exhibited by Pd; Pd/SiO_2 catalysts are more transparent and give well-defined CO adsorption bands (*10, 11*) compared with the more opaque and lower surface area Cu/ZnO system. The effects of Li promotion were also investigated.

EXPERIMENTAL

Catalysts

Two silica supports were used, Davison 57 and 59. Specifications were almost the same for both with a surface area of 300 m^2 g^{-1}, a pore volume of 1.0 cm^3 g^{-1} and an average pore diameter of 140 Å, the only difference being the particle size and a small variation in trace alkali-metal components shown in Table 1. Differences in particle size were eliminated by grinding the silicas to the same 14–20 mesh size before preparation.

Pd was added to these supports by either impregnation or ion-exchange methods. The impregnated catalysts were prepared by the incipient wetness technique using aqueous solutions of the Pd chloride and nitrate salt. After drying, each catalyst was calcined at 300°C for 2 h. Pd ion-exchanged catalysts were prepared by the following procedure: The required amount of $Pd(NH_3)_4(NO_3)_2$ solution was added to a slurry of silica gel and water. The water was alkalized by adding a few drops of NH_4OH to make the pH ~9.5. After mixing for 1 h, the silica was washed and filtered and, finally, calcined at 300°C for 2 h. For the Li-doped samples, Li was added as the hydroxide prior to the Pd impregnations.

The weight percentage Pd reported in the tables represents loadings calculated from the volume and concentration of the impregnation solutions. With ion-exchanged samples, post analysis by the inductively coupled plasma technique showed that the 1.5 and 5.0 wt% Pd actually contained 1.0 and 2.9 wt% Pd, respectively. Pd dispersion measurements were conducted on several representative samples by CO chemisorption. The method employed a pretreatment reduction at 350°C in H_2, and CO pulse adsorption at room temperature with a chromatographic detector system. Calculations were based on the assumption of one CO molecule per Pd atom. Results are shown in Table 2.

Reactor System

The reactor used in testing the methanol synthesis catalysts was a vertical $\frac{1}{2}$-in. stainless-steel tube enclosed in a hinged furnace. Cylinders CO and H_2 were fed into the system via pressure regulators and Brook's mass flow controllers. Silica gel traps in each gas line helped dry the gas and remove all possible traces of carbonyls.

TABLE 2

Typical Pd Dispersions

Catalyst	% Pd dispersed
1.5% Pd/SiO_2 57 (ion-exch.)	62
5.0% Pd/SiO_2 59 (ion-exch.)	17
5.0% Pd/SiO_2 57 (ex $PdCl_2$)	10
5.0% Pd/1.6% Li/SiO_2 57 (ex $PdCl_2$)	5
5.0% Pd/1.6% Li/SiO_2 59 (ex $Pd(NO_3)_2$)	5

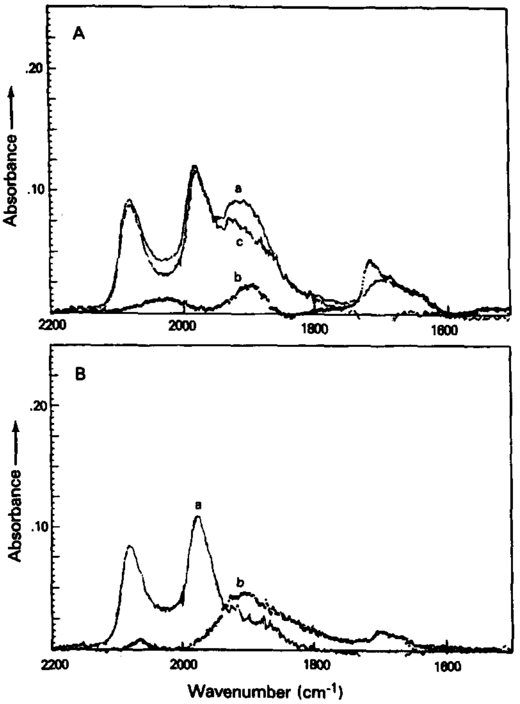

FIG. 1. Spectra of CO adsorbed on 5% Pd/SiO$_2$ 57 (ex PdCl$_2$). (A) Spectra showing "cooling" correction: (a) CO (2.3 Torr); (b) N$_2$ (2.3 Torr); (c) (a–b) corrected spectrum. (B) Spectra showing strongly and weakly held CO; (a) weakly held CO; (b) Strongly held CO (held after 5-min evac.).

The desired pressure was maintained at the reactor outlet by pneumatically operated pressure control valves. The product stream for this valve passed via a heated line to an in-line Varian 6000 G.C. This chromatograph analyzed the products and reactants (H_2, CO, CO_2, H_2O, N_2, CH_3OH, CH_3OCH_3, CH_4, C_2H_6, and C_3H_8). The outlet flow was measured by a wet-test meter.

Prior to running the reaction, each catalyst was pretreated *in situ* at 340°C for 2 h in flowing H_2. Some runs were made without prereduction, and the resulting activity was considerably lower, and only increased after running in the reducing conditions of the reactor for some time. Normally, the activity lined-out after 30-min running, and thereafter deactivation was slow. The reported activities were taken after 2 h from start-up. The catalysts tested all showed selectivities to methanol of over 90%. Several runs were made testing the reproducibility of the reactor and activities were found to be ±20% of their mean values at conversions below 1% and ±10% at conversions around 5%.

Infrared analyses were performed on a computerized IR Beckman 4260 as previously described (*14*). Corrections were applied for changes in background bands (arising from the support) caused by cooling of the sample when CO was admitted to the cell. The "cooling" corrections, particularly in the case of 5% Pd samples, were quite important and different conclusions would have been reached had they not been applied to the spectra. To permit such corrections, spectra were recorded before and after addition of dry nitrogen at pressures similar to those used for the CO additions. Using the computer, the "blank" bands produced by N_2 addition were then subtracted from those produced by addition of CO to the same sample. An example of this correction procedure is shown in Fig. 1A. The validity of this procedure was established by earlier work showing that similar "blank" bands could be produced by addition of helium or of hydrogen so that no actual adsorption of N_2 was responsible for these bands. One set of spectra was recorded with a Perkin–Elmer 1550 FTIR spectrometer.

RESULTS

Differences between catalysts prepared from the two silica supports 57 and 59 are quite clearly demonstrated in Table 3. In all cases, catalysts prepared from silica 59 showed higher activity than those prepared from silica 57. However, the increase was smallest with the Li-promoted catalyst, suggesting the differences in activity may arise out of differences in the amount of residual alkali-metal contaminant; however, analysis results failed to confirm this.

Differences in the mode of adding Pd to the support evidently made little difference in the subsequent activity of the catalyst as

TABLE 3

Variation in Silica Support

Catalyst	Method of Pd addition	% CO converted to MeOH
5% Pd/SiO_2 57	Impregnated $PdCl_2$	0.8
5% Pd/SiO_2 59	Impregnated $PdCl_2$	2.5
5% Pd/SiO_2 57	Ion-exchanged $Pd(NH_3)_4(NO_3)_2$	1.2
5% Pd/SiO_2 59	Ion-exchanged $Pd(NH_3)_4(NO_3)_2$	3.0
5% Pd/1.6% Li/SiO_2 57	Impregnated $PdCl_2$	4.6
5% Pd/1.6% Li/SiO_2 59	Impregnated $PdCl_2$	6.0

Note. Conditions: 500 psig, SV = 900 hr^{-1}, 275°C, and H_2: CO = 68.2:31.8. %Pd as added, not analyzed.

TABLE 4

Variation in Pd Addition

Catalyst	Method of Pd addition	% CO converted to MeOH
5% Pd/SiO_2 59	Impregnated $PdCl_2$	2.5
5% Pd/SiO_2 59	Impregnated $Pd(NO_3)_2$	2.0
5% Pd/SiO_2 59	Ion-exchanged $Pd(NH_3)_4(NO_3)_2$	2.0
1.5% Pd/SiO_2 57	Impregnated $PdCl_2$	0.9
1.5% Pd/SiO_2 57	Impregnated $Pd(NO_3)_2$	0.8

Note. Conditions as in Table 3.

TABLE 5

Effect of Pd Loading on Activity

Catalyst	Method of Pd addition	% CO converted to MeOH
1.5% Pd/SiO_2 59	Ion-exchanged $Pd(NH_3)_4(NO_3)_2$	3.0
5.0% Pd/SiO_2 59	Ion-exchanged $Pd(NH_3)_4(NO_3)_2$	2.0
1.5% Pd/SiO_2 57	Impregnated $PdCl_2$	0.9
5.0% Pd/SiO_2 57	Impregnated $PdCl_2$	0.8

Note. Conditions as in Table 3.

TABLE 6

Effect of Lithium Promotion

Catalyst	Method of Pd addition	% CO converted to MeOH
5% Pd/SiO_2 57	Impregnated $PdCl_2$	0.8
5% Pd/SiO_2 57 + 1.6% Li	Impregnated $PdCl_2$	4.6
5% Pd/SiO_2 59	Impregnated $PdCl_2$	2.5
5% Pd/SiO_2 59 + 1.6% Li	Impregnated $PdCl_2$	6.0
5% Pd/SiO_2 59	Impregnated $Pd(NO_3)_2$	2.0
5% Pd/SiO_2 59 + 1.6% Li	Impregnated $Pd(NO_3)_2$	5.0
1.5% Pd/SiO_2 59	Ion-exchanged $Pd(NH_3)_4(NO_3)_2$	3.0
1.5% Pd/SiO_2 59 + 1.6% Li	Ion-exchanged $Pd(NH_3)_4(NO_3)_2$	4.3

Note. Conditions as in Table 3.

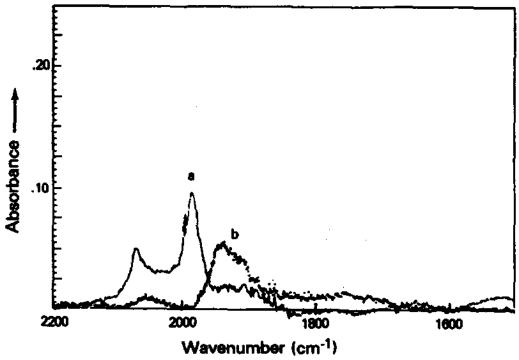

FIG. 2. Spectra of CO adsorbed on 5% Pd/SiO_2 59 (ex $Pd(NO_3)_2$): (a) weakly held CO; (b) strongly held CO (held after 5-min evac.).

shown by the data of Table 4. These data were obtained on catalysts ion-exchanged with amino nitrate complex or impregnated with either the nitrate or chloride salt. Similar lack of variation in activity was observed by changing the Pd loading from 1.5 to 5.0% as seen in Table 5, which can be partially explained by a decrease in dispersion as indicated by the subsequent absorbance of the IR bands.

Significant differences were observed when Li was added as a promoter. Table 6 shows Li always increased the activity for every catalyst type used. The increase, however, was smallest for the Pd ion-exchanged on silica 59 possibly since without Li this catalyst had a higher activity, but, also, this smaller increase could be a result of the absence of residual alkali in the support.

Infrared Spectra

Figures 1 to 5 represent IR spectra of CO adsorbed on some of the catalyst samples whose activities were measured in an attempt to relate catalyst performance to catalyst surface properties. Each spectrum is characterized by bands near ~2075 and 1975 cm^{-1} corresponding to weakly held CO previously assigned to linear and bridged bonding of CO on Pd, respectively (*15*). The spectra after evacuation and, therefore, representing strongly held CO, typically show less intense bands near 2060 and 1900 cm^{-1}, again reflecting linear and bridged CO. Additional bands can also be seen. These probably reflect various bridged CO species held on different crystal faces (*15*). Figures 1A and B show spectra of CO on 5% Pd/SiO_2 57 made by the impregnation of the chloride salt. Figure 1A demonstrates the application of the "cooling correction" which was used with most of the following spectra, while Fig. 1B shows the separation of the corrected spectra into strongly and weakly held CO bands.

Figure 2 shows the corresponding strongly and weakly held CO spectra on 5% Pd/SiO_2 59 made by the impregnation of the nitrate salt. The general features of both Figs. 1 and 2 are similar, but some differences are observed in the relative intensities of the bands near 2075 and 1975 cm^{-1} corresponding to weakly held linear and bridge-bonded CO. Differences can also be seen in the frequencies of bands caused by strongly held CO remaining after evacuation. A small difference was observed in the relative activities of these two catalysts; the catalyst in Fig. 2 showing the lower intensity CO bands had, however, a slightly higher activity.

Spectra of CO on a 1.5% Pd/SiO_2 catalyst, corresponding to the same support and mode of addition of Pd as the catalyst in Fig. 1 except for the loading level, are shown in Fig. 3. These spectra were the

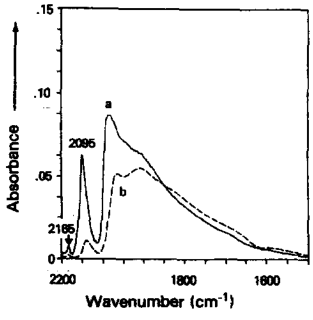

FIG. 3. Spectra of CO adsorbed on 1.5% Pd/SiO_2 57 (ex $PdCl_2$) [FTIR]: (a) CO (2.0 Torr); (b) strongly held CO (after 5-min evac.). (No correction was applied to these spectra.)

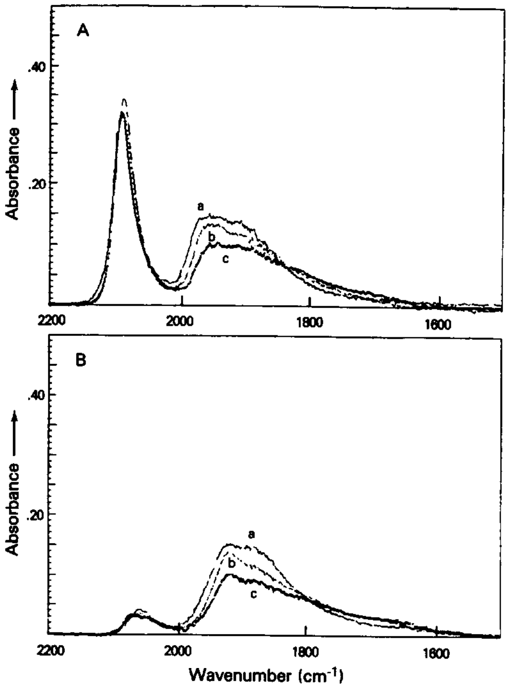

FIG. 4. Effects of Li on 1.5% Pd/SiO$_2$ 59 (ion-exchanged). (A) Spectra of CO (2.1 Torr, corrected) on catalysts containing the following Li contents: (a) 0%; (b) 0.7%; (c) 1.6%. (B) Spectra of CO retained after 5-min evac. on the same catalysts (a, b, and c).

only ones shown by FTIR, and the general features are very similar; however, an additional band was observed here at 2165 cm^{-1}. Additional experiments using both FTIR and dispersive IR with other samples had demonstrated the equivalency of the two methods.

Figure 4 shows the effect of Li on the CO/Pd spectra obtained for 1.5% Pd ion-exchanged on Davison 59 silica. (Note change in absorbance scale.) In the case of Li-free catalyst, the spectrum of CO on the catalyst shows significant differences from those on the impregnated catalysts. A much more intense linear CO band and a relatively weaker bridge-bonded CO band are observed. However, little difference was observed in activity. No difference is seen in the linear CO bands (2060 and 2090 cm^{-1}) when Li is present. Only a slight difference exists between the bridged CO bands, yet a small increase in activity was noted. The strongly held bridged CO bands in the range 1850–1950 cm^{-1} appear to be progressively decreased in intensity and shifted to lower frequencies as Li content increases.

Figure 5 shows spectra of CO on the catalysts of Figs. 1 and 2, respectively, after the addition of Li. Comparison of the spectra with and without Li (B and D versus A and C) shows very little effect of Li on the CO spectra in the region above 1950 cm^{-1}. In the region below 1950 cm^{-1}, however, there was a significant increase in both weakly and strongly held bridged CO. There was a large corresponding increase in

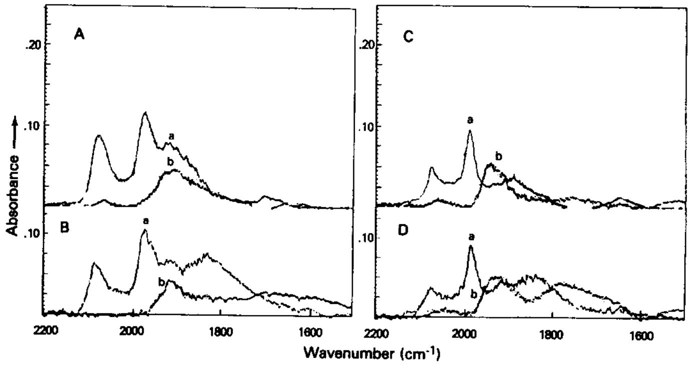

FIG. 5. Effects of Li on 5% Pd/SiO$_2$ (impregnated catalysts). In all cases (a) spectra of CO (2.3 Torr, corrected); (b) strongly held CO (held after 5-min evac.). (A) 5% Pd/SiO$_2$ 57 (ex PdCl$_2$) (from Fig. 1). (B) Same as in A with 1.6% Li. (C) 5% Pd/SiO$_2$ 59 (ex Pd(NO$_3$)$_2$) (from Fig. 2). (D) Same as C with 1.6% Li.

activity by factors of 6 and 3, respectively, when Li was present.

DISCUSSION

Spectra of CO on Pd have been thoroughly discussed elsewhere (*15*). It was initially hoped, and expected, that among the variety of different types of bands observed for CO adsorbed on silica-supported Pd some correlation would be found with methanol synthesis activity. No obvious correlation was, in fact, apparent. Some previous speculation appears to have been excluded by the evidence, however, and possible explanations for Li promotion can be offered.

Careful attention was paid to possible adsorption of CO on Pd^{n+} ions, which would have been expected to give bands above 2100 cm^{-1}, and even, by analogy with Ni^{2+}, as high as 2195 cm^{-1} (*16*). A band suggestive of Pd^{n+} adsorption sites was seen in only one instance. This was on a 1.5% Pd catalyst. After prereduction at 300°C and addition of CO (as shown, Fig. 3), this catalyst showed a very weak band at 2165 cm^{-1} which probably reflects CO held on Pd^{2+} ions. This catalyst was, however, one of the least active (see Table 5). Unreduced Pd would not be expected under reaction conditions in any case, but the fact that activity was found to increase with increasing prereduction of the catalysts and, initially, with increasing time on stream strongly argues that Pd^{n+} sites are not, as postulated by Ponec *et al.* (*9, 13*), the active sites.

The infrared spectra show that Li addition has a small but definite effect on the bridged bonding of CO to Pd. Such bonding presumably occurs mainly on exposed faces of Pd crystallites. The effect could be either electronic or structural in nature. The Li, in a partial overlayer on a Pd surface, could affect the electronic properties of adjacent Pd atoms, changing their subsequent adsorption of CO. Alternatively, Li might promote exposure of crystal faces different from those normally present. The existence of an effect of Li on bridge bonding of CO does not, of course, mean that this is the factor responsible for activity promotion by Li. The data generally show no obvious correlation of activity with any particular type of CO bonding as revealed by the frequency and intensity of infrared bands arising from adsorbed CO.

The fact that wide differences in the types of CO adsorption on reduced Pd made so little difference in catalyst activity while marked differences in activity were observed on catalysts with generally similar CO adsorption sites suggests that some factor other than CO binding could well be of major importance. This could be the ability of the support to heterolytically dissociate hydrogen to form hydroxyl and hydride species on the surface. Zinc oxide is well known for its ability to do this and evidence has also been presented that MgO and La_2O_3 can similarly dissociate hydrogen. Work in this laboratory has shown that alumina possesses a few sites which exhibit this behavior. The ability to form surface hydride may be the essential feature needed for methanol synthesis in addition to the nondissociative adsorption of CO. The effect of Li may be to provide surface sites on silica on which such dissociation can occur more readily. Further work is planned to investigate these possibilities. Obviously, the types of sites available for CO and H_2 adsorption under reaction conditions may differ from those seen on fresh catalysts. *In situ* IR studies under reaction conditions could shed additional light on this subject. Such studies are also planned.

CONCLUSIONS

Major differences in the IR spectra of adsorbed CO on fresh catalysts which could reflect changes in both the electronic and structural properties of the supported Pd are seen, where no significant changes are observed in catalyst activity. Yet, where only relatively slight differences in the CO spectra are observed, as is the case following Li addition, significant differences do occur in activity. In short, no clear relationship exists between the character of the Pd as shown by CO adsorption and its catalytic activity. Li promotion of methanol synthesis with Pd catalysts apparently affects CO adsorption on Pd by changing the nature of some sites for bridged adsorption of CO, but it may also serve some independent function, possibly promoting dissociative adsorption of H_2. Since marked changes in Pd catalyst activity occur on changing the nature of the support (*11*, *12*), this second function may usually be provided by the support.

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