

Modified Chromium/Silica Gel Catalysts: An FTIR Study of the Addition of Alkali Metal Ions

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Addition of alkali metal ions to the Phillips catalyst has a strong negative influence on the amount of chromium(II) surface ions detectable in low-temperature FTIR spectra of CO adsorbed on various chromium(II) species. However, small additions of Li and Na (below 0.1 or 0.05 mmol g⁻¹ silica gel, respectively) have no adverse effect, while such an 'offset' was not observed for K, Rb or Cs. From the decrease of the amount of chromium(II) surface ions it is concluded that Li forms Li₂CrO₄ during the preparation of the samples and K, Rb and Cs alkali metal dichromates. Na forms both compounds. Surprisingly, a small shift of 1 to 2 cm⁻¹ to higher wavenumbers is observed for the CO bands at 2047, 2035 and 2027 cm⁻¹, indicating a decrease of the electron density at the chromium(II) ions. This effect is explained in the discussion.

The Phillips catalyst [chromium(VI) on silica gel]¹ for the polymerization of ethylene is very important in the chemical industry, because 40 % of high-density polyethylene² is produced with the help of this catalyst. Since 1968 it has been known that the catalytically active chromium species have the oxidation number two and are coordinatively unsaturated.³ Later it was found that several active chromium species^{4–10} exist, of which the so-called A species (oxidation number 2, coordination number 2) is the major one present after high-temperature activation (800 °C, O₂) and reduction at lower temperatures (350 °C, CO), together with a small amount of the chromium(II) C species (oxidation number 2, coordination number 3). IR spectra of CO adsorbed on these surface species show two groups of CO bands between 2178 and 2200 (terminal CO) and 2030 to 2160 cm⁻¹ (bridging CO) at room temperature and low temperature (–120 °C), respectively.

The Phillips catalyst has been successfully modified either by using other support materials (amorphous AlPO₄)^{11–14} or modifying the silica gel with titanium^{15–20} or fluorine.^{21–25} Recent investigations in our laboratory showed that these modifications yield distinctly different CO IR spectra, which allow a determination of the active species distribution and their characterization.^{26–32}

The addition of alkali metal ions to the Phillips catalyst³³ and its effects on the chromium surface compounds may therefore be best studied by IR spectroscopy of adsorbed CO; in addition, such an investigation might yield some information about the coordination of surface alkali metal ions.³⁴ It should be kept in mind that alkali metal ions, mainly Na, are usually present as contaminants in silica gel produced by precipitation from Na₄SiO₄ and H₂SO₄.

Experimental

Silica gel GRACE/Davisson 952 (specific surface area 300 m² g⁻¹, pore volume 1.6 cm³ g⁻¹) was used as the support without further purification. The samples were prepared by impregnating the support with 0.5 wt. % Cr (0.1 mmol g⁻¹ silica gel, as a CrO₃–water solution) and either 0.1, 0.2 or 0.4 mmol alkali metal chloride per g silica gel. The samples, denoted Li1 to Cs4, were dried at 120 °C in air.

65 mg of the samples were pressed into a disc with a diameter of 2 cm and placed in an IR cell.³⁵ The cell was then heated to 800 °C under vacuum and filled with O₂ (10 min). After being cooled to 350 °C the IR cell was evacuated and the sample reduced with CO for 15 min. The CO was removed by evacuation at 300 °C and the first FTIR spectrum recorded at room temperature. After the cell had been filled with 10 kPa CO and cooled to –120 °C a second spectrum was recorded. The IR cell was evacuated again at room temperature and then treated with a 'heat gun' for 1 min (400 °C). After both steps a further IR spectrum was recorded. The first spectrum was usually subtracted from the CO spectra.

The FTIR spectra were collected with a Nicolet 20 SXC spectrometer. The resolution was set to 2 cm⁻¹ and 1024 scans were averaged. For a quantitative evaluation of the FTIR spectra of the adsorbed CO species the curve-fitting procedure of SpectraCalc was performed, usually with no fixed parameters.³² In order to check the quality of the curve fitting, the positions of the fitted bands were compared with the positions obtained from the second derivative of the CO spectra calculated on the data station of the Nicolet 20 SXC. A difference of less than ±1 cm⁻¹ in the positions was deemed sufficiently accurate (see Results).

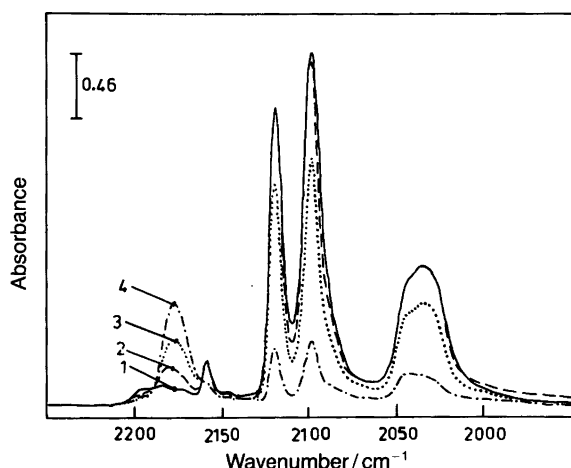


Fig. 1. FTIR spectra of CO adsorbed at low temperatures (-120°C) on chromium(II)/silica gel samples modified by Li. Spectrum (1) is from a sample without Li, (2) with 0.1 mmol Li/g, (3) with 0.2 mmol Li/g and (4) with 0.4 mmol Li/g.

Results

Fig. 1 shows the low-temperature (-120°C) IR spectra of CO adsorbed on the chromium/silica gel catalyst modified with lithium. In all spectra one observes the three CO IR bands from bridging CO at 2120, 2100 and 2035 cm^{-1} . The addition of small amounts of lithium (0.1 mmol) has almost no effect on the spectrum (spectrum 2 cf. spectrum 1). The only differences are that the weak CO band at 2200 cm^{-1} from CO on chromium(III) ions⁷ has approximately half its intensity left and that a new CO band appears at 2178 cm^{-1} which has been previously assigned to CO adsorbed on lithium surface ions.³⁴

Addition of more lithium (0.2 mmol g^{-1} , spectrum 3, Fig. 1) enhances these two effects, and the CO band at 2180 cm^{-1} shifts to lower wavenumbers (2176 cm^{-1}). The low-temperature IR bands of CO decrease by some 20% and the shoulder at 2045 cm^{-1} becomes more visible. The latter result is characteristic of the chromium(II) C species. In other words, the relative amount of this surface species is increased in this sample. The highest amount of added lithium (0.4 mmol) has a more drastic effect on the IR bands of CO, which are now smaller by some 80%. The IR band of CO at 2045 cm^{-1} is now even higher than the one at 2035 cm^{-1} . Because the latter CO band is obviously broader than that at 2045 cm^{-1} the two CO bands around 2040 cm^{-1} may have similar intensities. It is also observed that the CO band from CO adsorbed on lithium at 2176 cm^{-1} again increases in this sample, but that this band is not exactly twice as large compared to spectrum 3 for the sample with only half the amount of lithium.

As Fig. 2 shows, addition of Na to the reduced Phillips catalyst gives a more pronounced effect in the CO spectra than addition of Li. With only 0.1 mmol Na g^{-1} silica gel the CO bands at 2120, 2100 and 2035 cm^{-1} decrease (spectrum 2, Fig. 2) and these three bands have vanished com-

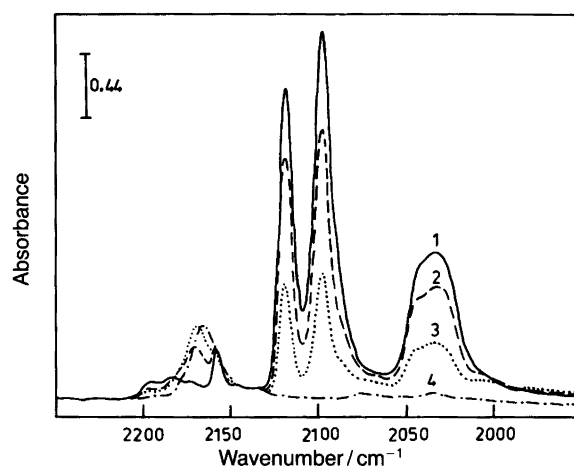


Fig. 2. FTIR spectra of CO adsorbed at low temperatures (-120°C) on chromium(II)/silica gel samples modified by Na. Notation of spectra as in Fig. 1.

pletely after addition of 0.4 mmol Na (spectrum 4). Only two weak CO bands are now present below 2143 cm^{-1} at 2077 and 2036 cm^{-1} . A small additional CO band is seen at 2005 cm^{-1} . A shift to lower wavenumbers is observed for the IR band of CO adsorbed on Na from 2172 (spectrum 2) to 2171 (spectrum 3) to 2168 cm^{-1} (spectrum 4) with increasing Na concentration. However, no linear increase in its intensity is found.

As Fig. 3 shows, the above trends are even stronger after addition of K. The IR band from CO adsorbed on K shifts to lower wavenumbers from 2164 to 2162 cm^{-1} . Similar spectra are also observed in Figs. 4 and 5 with addition of Rb and Cs, respectively. In all these cases a weak CO IR band is seen near 2000 cm^{-1} .

In the IR spectra of the surface silanol group at 3745 cm^{-1} (not shown), it was observed that the intensity of this

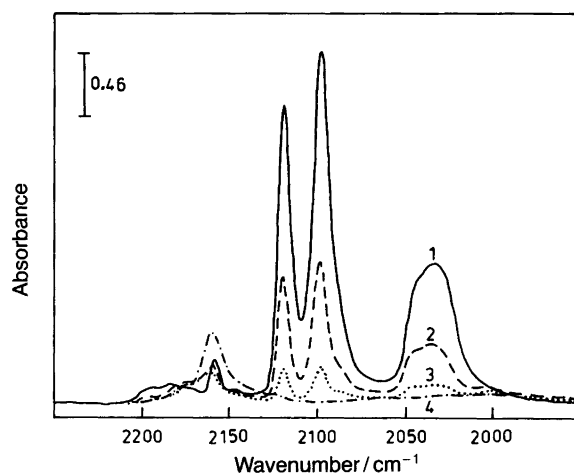


Fig. 3. FTIR spectra of CO adsorbed at low temperatures (-120°C) on chromium(II)/silica gel samples modified by K. Notation of spectra as in Fig. 1.

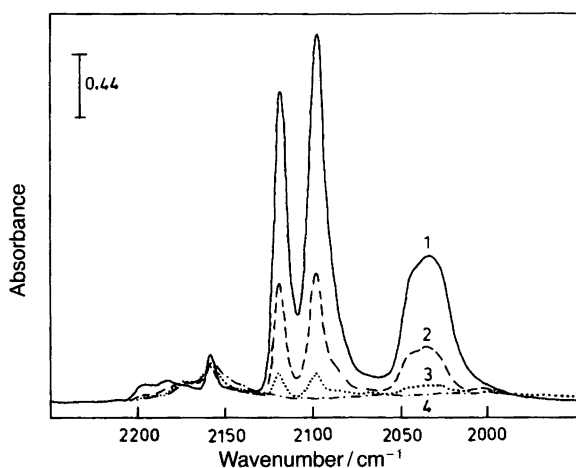


Fig. 4. FTIR spectra of CO adsorbed at low temperatures (-120°C) on chromium(II)/silica gel samples modified by Rb. Notation of spectra as in Fig. 1.

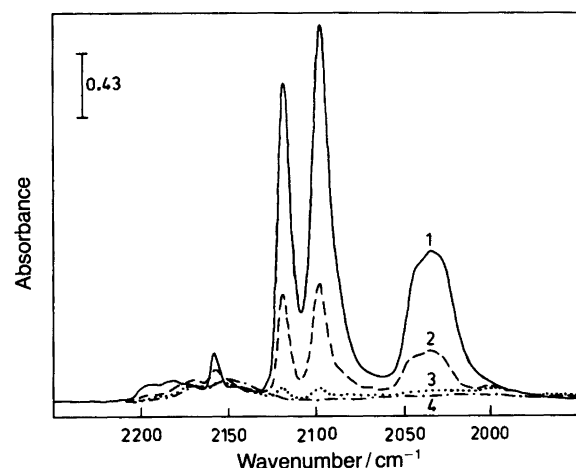


Fig. 5. FTIR spectra of CO adsorbed at low temperatures (-120°C) on chromium(II)/silica gel samples modified by Cs. Notation of spectra as in Fig. 1.

band decreased only by 20–30% after addition of the largest amount of alkali metal ion, and neither a linear relationship with the alkali metal concentration nor any significant shift of the OH band was found.

Fig. 6 shows the positions of the three CO bands at 2046, 2035 and 2026 cm^{-1} obtained from the second derivative (\times) of the low-temperature CO spectra and from curve fitting (\circ).³² Generally the two values from these different procedures are within $\pm 1 \text{ cm}^{-1}$ of each other, which is an indication of the rather good quality of the curve-fitting and the reliability of these results. Only a slight shift of about 1–2 cm^{-1} to higher wavenumbers is observed for these three CO bands after addition of alkali metal ions.

Fig. 7 shows the total integrated area of the three CO bands at 2046, 2035 and 2026 cm^{-1} as derived from curve fitting (\times). The circles (\circ) in Fig. 7 are calculated by addition of the integrated absorbance of the CO IR band near 2000 cm^{-1} to that of the former three CO bands. The quantitative evaluation confirms that the alkali metal ions decrease the number of coordinatively unsaturated chromium(II) surface ions according to their weight. The effect levels off, however, for K, Rb and Cs at 30% (0.1 mmol alkali metal ion g^{-1}) and below 10% (0.2 mmol alkali metal ion g^{-1}). The highest alkali metal ion concentration employed (0.4 mmol g^{-1} with 0.1 mmol Cr g^{-1}) yields the three low-temperature IR bands of CO only for Li. A linear relationship between the decrease of these CO bands [i.e. the number of coordinatively unsaturated chromium(II) surface ions] and the Li concentration is observed in Fig. 7. However, the linear extrapolation of this to concentrations lower than 0.1 mmol g^{-1} shows that in the case of Li a very small effect, or none at all, will be observed at small additions of this alkali metal ion. For low amounts of Na (below 0.5 mmol g^{-1}) a smaller influence on the number of chromium surface ions should be observed than expected from the linear extrapolation. For the other three alkali metal ions the full effect will decrease the number of

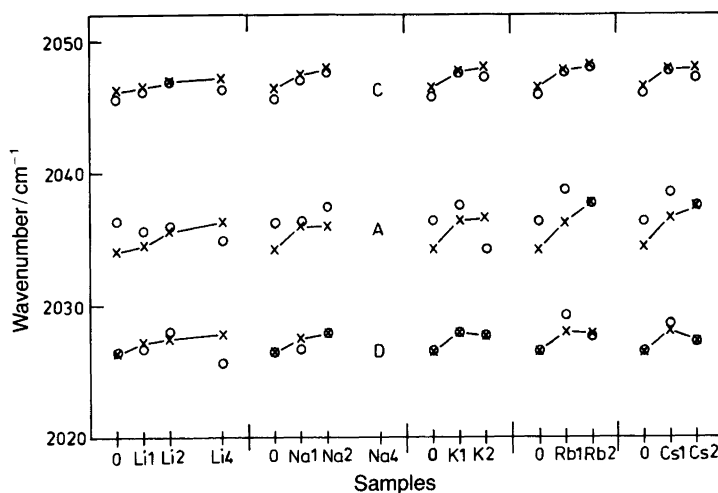


Fig. 6. The position of the three CO IR bands at 2047, 2035 and 2027 cm^{-1} for chromium(II)/silica gel samples modified by alkali metal ions. The sample without addition of alkali metal is denoted 0. The crosses (\times) indicate values obtained from the second derivative of the spectra and the circles (\circ) values from curve-fitting. The difference between these values is a measure of the quality of curve-fitting. The Letters C, A and D indicate chromium(II) surface species.

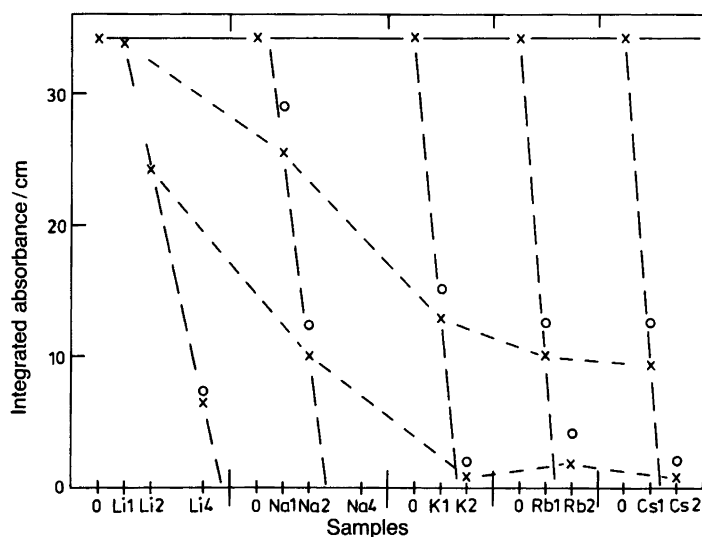


Fig. 7. The integrated intensity of the three CO IR bands at 2047, 2035 and 2027 cm^{-1} plotted versus the chromium(II)/silica gel samples modified by alkali metal ions (\times). The circles (\circ) are calculated by adding the integrated intensity of the Co band near 2000 cm^{-1} to the previous value.

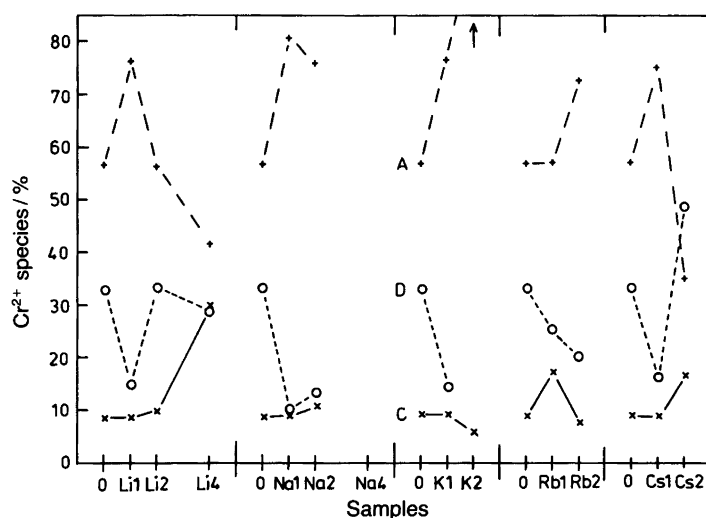


Fig. 8. The relative amount of the chromium(II) surface species A (+), C (\times) and D (\circ) plotted versus the chromium(II)/silica gel samples modified by alkali metal ions.

coordinatively unsaturated chromium(II) surface ions even at low alkali metal ion concentrations.

The percentage of the three chromium(II) species A, C and D (see discussion) is shown in Fig. 8 as calculated from the curve fitting of the three IR bands of CO at 2036 (A), 2046 (C) and 2027 cm^{-1} (D), respectively. A small addition of Li increases the amount of A species and similarly decreases the amount of the D species. Larger Li concentrations decrease the relative part of the A species and increase the C species. The first effect is also observed with Na and K. This quantitative evaluation is in agreement with the qualitative inspection of the CO spectra above (Fig. 1).

Discussion

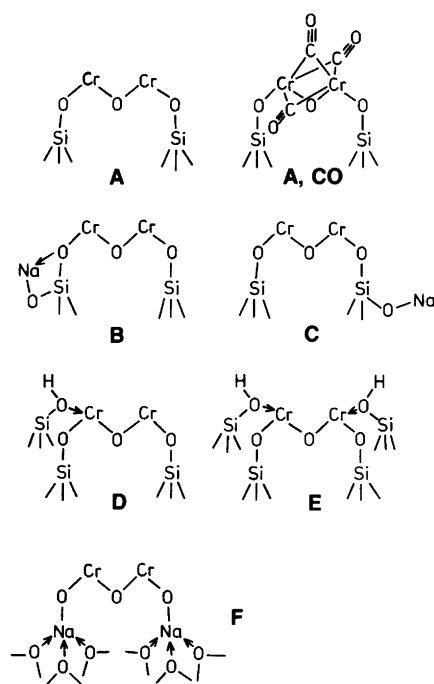
As already mentioned in the introduction, the silica gels prepared by precipitation from Na_2SiO_4 and H_2SO_4 contain small amounts of Na. These Na cations, mainly on the surface of the support, give a weak IR band for adsorbed CO (2174 cm^{-1}) at low temperatures (spectrum 1 in Figs. 1–5, especially Fig. 2). For the Grace 952 silica gel used for this investigation, the concentration of Na surface ions is in the order of 0.02 mmol Na g^{-1} silica gel. In view of the linear decrease of chromium(II) surface species at higher Na concentrations (Fig. 7) this small amount of Na will

have no influence on the activity of polymerization of the Phillips catalyst. Indeed it may be beneficial by suppressing the formation of polymerization-inactive chromium(III) surface ions, as seen by the decrease of the CO band at 2200 cm^{-1} in Fig. 2. The manufacturers of silica gels for polymerization catalysts may have arrived at this result long ago by a trial-and-error procedure.

The suppression of the formation of chromium(III) surface ions by addition of alkali metal ions can also explain the increase in the polymer growth rate and number of active sites by some 10% observed previously.³³ A larger effect than observed above would be expected there because that support had been purified by washing with conc. HCl in order to remove alkali metal surface ions.

Generally, the alkali metal ions can either (i) occupy independent surface sites or (ii) form alkali metal chromates during the impregnation and drying at 120°C . The alkali metal chromates will probably decompose to chromium(III) oxides at higher temperatures and thereafter be inactive as polymerization sites. From Fig. 7 it can be concluded that Li cations favour independent surface sites (i), and only with a surplus of these ions can formation of Li chromates occur. The small ionic radius of Li cations may be the cause of their incorporation into the silica gel surface. A similar but much smaller effect is also observed for Na surface cations. The addition of 0.1 mmol g^{-1} of K, Rb and Cs decreases the amount of coordinatively unsaturated chromium(II) surface ions by $> 50\%$. Because the chromium concentration is 0.1 mmol g^{-1} , such an effect would be expected, if mainly alkali metal dichromates (e.g. $\text{K}_2\text{Cr}_2\text{O}_7$) and no alkali metal monochromates (e.g. K_2CrO_4) are formed. The slope of the line with long dashes in Fig. 7 connecting the alkali metal samples of one element is smaller for Li. This is an indication that more than one Li ion is necessary to remove one chromium(II) surface ion, and is probably due to the formation of Li chromate (Li_2CrO_4). Again Na shows behaviour that is between the two extremes: Li on one hand and K, Rb and Cs on the other.

The position of the three CO bands (structure A,CO in Scheme 1) calculated from the second derivative increases slightly by $1\text{--}2\text{ cm}^{-1}$ (Fig. 6) on addition of electron-releasing alkali metal ions. The increase indicates a lower electron density on the chromium(II) surface ions.³⁰ This is somewhat surprising, because a shift in the same direction, although stronger, has been observed on addition of electron-withdrawing elements such as fluorine (5 cm^{-1})^{31,32} and phosphorus (7 cm^{-1} in AlPO_4).³⁰ An explanation of this effect may be that alkali metal ions coordinate to the free electron pair of oxygen atoms binding between Cr and Si, as shown in structure B in Scheme 1, and do not bind only to oxygen atoms as shown in structure C. A consequence of this explanation is that alkali metal ions on the silica gel surface will generally have higher coordination numbers than one, and are not sitting on top of oxygen atoms. This argument may also help one understand why the number of



Scheme 1.

surface hydroxyl groups is relatively little affected by the addition of alkali metal ions.

The arithmetic mean of the shift for all samples in Fig. 6 is slightly higher for the band near 2035 cm^{-1} (2.11 cm^{-1}), than for the other two (2046 cm^{-1} : 1.36 cm^{-1} and 2027 cm^{-1} : 1.17 cm^{-1}). Additional surface hydroxyl groups coordinating to the chromium(II) ion as shown in structures D and E in Scheme 1 (CO ligands omitted) can smooth the effect of alkali metal ion addition.

The small IR band of CO at low temperatures near 2000 cm^{-1} may be from bridging CO adsorbed on chromium(II) surface ions, as shown in structure F. Electron-releasing alkali metal ions directly bonded to Cr-O-groups should induce such an effect on the CO IR band. A drastic shift to lower wavenumbers of the CO band from terminally adsorbed CO has been observed on AlPO_4 and has been interpreted as due to Cr-O-Al bonds.³⁰ In agreement with this interpretation and with the one above for the formation of Li_2CrO_4 a relatively weak CO band at 2000 cm^{-1} is observed for the Li samples compared to the others (Fig. 7). However, complementary CO from terminally adsorbed CO between 2170 and 2160 cm^{-1} could not be identified on any of the alkali metal samples.

No consistent trends in the relative amounts of the different chromium(II) species A, C and D on addition of alkali metal ions are seen in Fig. 8. A trend in decreasing the D species seems to exist for Na, K, Rb and Cs and the C species seems to be relatively little affected. With addition of fluorine to the Phillips catalyst, however, a significant decrease of the C and D species of chromium(II) surface ions has been observed.³¹

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