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ACID-BASE PROPERTIES OF ALKALI PROMOTED CHROMIA-ALUMINA CATALYSTS

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Infrared study of pyridine and pyrrole adsorption and catalytic activity measurements have shown that alkali promotors eliminate the Lewis acidity, increase the strength of the surface basic sites and increase the dehydrogenation/dehydration activity ratio of Cr_2O_3-Al_2O_3 catalysts in the following sequence : Li,Na,K,Rb,Cs. Dissolution experiments indicate that these effects originate from the formation of a superficial chromate phase.

Previous investigations in the Cr_2O_3-Al_2O_3 system have indicated that alkali promotors enhance the catalytic activity in the dehydrogenation reaction of isobutane. (1,2). While lithium and sodium ions have little influence, the effect of potassium rubidium and cesium is very pronounced. Physico-chemical studies of this system have shown that the active promotors are segregated, from the bulk to the outer layers, with chromium ions to form a superficial chromate phase, the catalyst being in its oxidized form. This phase can be eliminated by washing, whereby the catalyst recovers an activity similar to that of Cr_2O_3-Al_2O_3 (2).

The purpose of this work is to characterize the acid and basic properties of these solids in order to correlate them with their catalytic activity. Methods which have been successful for other systems have been applied. They combine the infrared monitoring of the adsorption of probe molecules (3,4) with a catalytic test reaction (5,6). Adsorption of pyridine is used to characterize the surface acidity, while the perturbation of the NH vibration of pyrrole by H bonding allows characterization of the basic strength of the solid. The ratio of dehydrogenation/dehydration products obtained in the reaction of 4-Methyl pentan-2-ol may be correlated to the relative number of basic and acid sites (7).

The samples studied are the same as those previously described (1). They contain 7.5 mol % of Cr_2O_3 and 2.5 mol % of alkali oxides. Partial dissolution of the superficial chromate phase of the potassium promoted catalyst was performed by stirring 0.2 g of the solid in 200 cm^3 distilled water for 20 h at room temperature. The solid was then filtered and dried before being studied.

All details concerning sample preparation, instrumentation and instrumental conditions for the infrared study of the adsorption of probe molecules and the catalytic test reaction have been reported elsewhere (3-6).

Fig. 1 shows typical spectra of pyridine adsorbed on various samples outgassed at 600°C. Before adsorption, large bands are observed at 1440-1445 cm^{-1} and

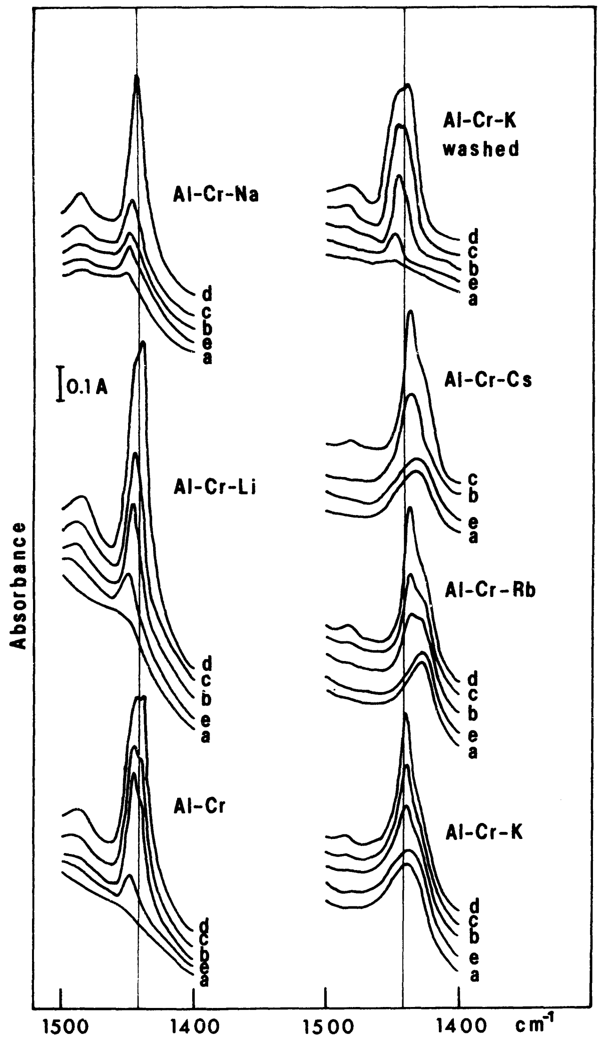

Fig. 1 : Infrared spectra of pyridine absorbed on the indicated samples. Spectra obtained before adsorption (a), after adsorption of pyridine in increasing amounts (b,c,d) and after subsequent outgassing at 150°C (e).

1610-1620 cm^{-1} for the K,Rb and Cs samples which are due to residual coke species originating from the synthesis of the catalysts.

After adsorption of pyridine, the non-promoted chromia-alumina catalyst gives two bands around 1445 cm^{-1} ; first one appears at 1450 cm^{-1} for small adsorbed amounts, the other appears at 1440 cm^{-1} for higher adsorbed amounts. The first band is attributed to pyridine coordinated to a Lewis site, the second is due to physisorbed pyridine (3). After subsequent outgassing at 150°, only the band due to Lewis acid-bound pyridine remains.

Comparison of the spectra of the various promoted samples, shows that the component revealing Lewis site at 1450 cm^{-1} disappears progressively in the Li,Na,K,Rb and Cs sequence (Fig.1) indicating that the Lewis sites have been eliminated. Even though this is qualitatively confirmed by the progresive disappearance of the 1620 cm^{-1} band, also attributed to coordinated pyridine (3), this region is less appropriate to further interpretations due to superposition of this band of weak intensity with the band of the residual coke species.

Adsorption of pyridine on the washed K promoted catalyst shows the band at 1450 cm^{-1} which was not observed on the original sample (Fig.1). This suggests that the elimination of the Lewis sites by the alkali promotors is due to the formation of the superficial chromate phase which is not acidic.

The spectra obtained in the OH and NH stretching vibration region after outgassing at 600°C and adsorption of pyrrole are given in Fig.2.

Before adsorption, pure chromia-alumina shows two OH bands at 3595 and 3705 cm^{-1}. Alkali promoted samples give strongly modified spectra : bands are observed at 3725,3720,3705,3703 and 3698 cm^{-1} for the Li,Na,K,Rb and Cs catalysts respectively ; for the Li and Na samples, a second band similar to that of pure chromia-alumina seems still to exist at 3705 cm^{-1}, but for all the promoted samples, the 3595 cm^{-1} does not appear.

After adsorption of pyrrole, some of the OH groups are perturbed through H

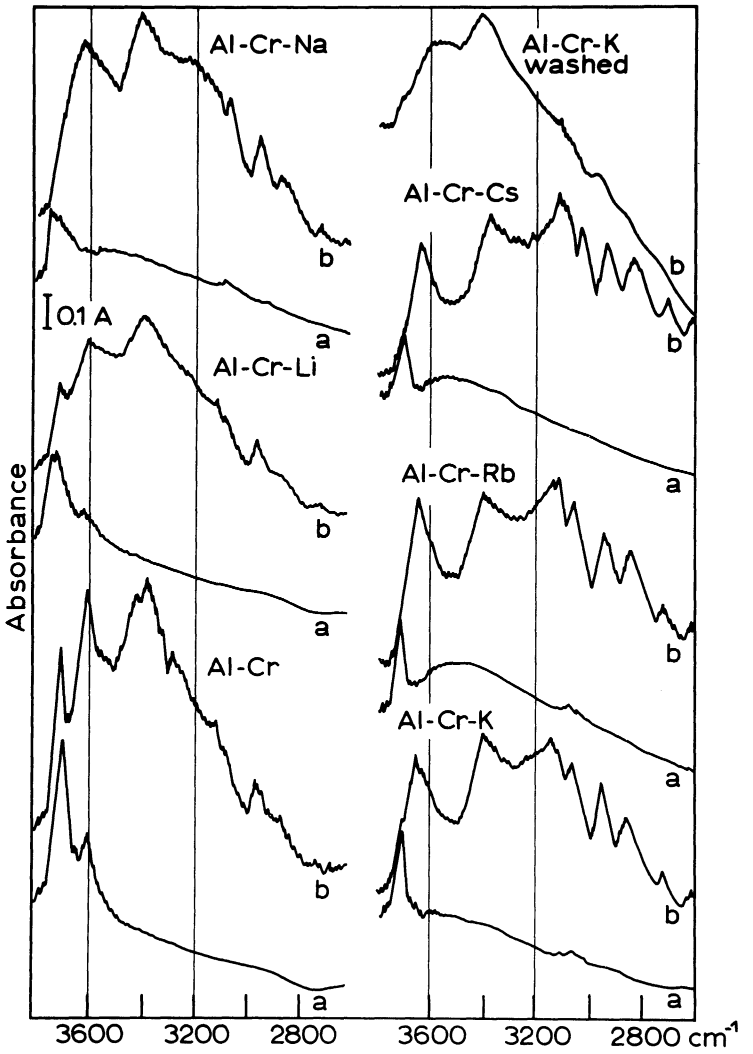

Fig. 2 : Infrared spectra of pyrrole adsorbed on the indicated samples. Spectra obtained before adsorption (a) and after adsorption of pyrrole (b).

bonding with the ring of pyrrole, giving bands around 3600 cm^{-1}. Nevertheless, the presence of sharp, well defined bands at 3700 and 3600 cm^{-1} in the spectra obtained after adsorption of pyrrole on pure chromia-alumina suggests that part of these hydroxyl groups are internal hydroxyls inaccessible to H bond acceptors. This has been confirmed through adsorption of benzene and pyridine.

Comparison of the spectra of Fig. 2 indicates that the acid strength of the hydroxyl groups which are accessible to H bonding decreases with each promotor in the order Li,Na then K,Rb and Cs, as revealed by a shift towards 3650-3660 cm^{-1} of the 3600 cm^{-1} perturbed OH band. These results are very similar to those obtained previously for pure alumina poisoned by Na or K impregnation (8).

The NH band appearing at 3400 cm^{-1} is due to autoassociated pyrrole (4). The bands wich appear below 3000 cm^{-1} have no clear attribution, but their intensities always appear very high for basic solids (4,8).

The NH band due to H bonding of pyrrole with a basic site appears as a shoulder at 3260 cm^{-1} for the pure chromia-alumina catalyst. This frequency is similar to that obtained for pure aluminas (4) indicating that the strength of the basic sites is similar. For alkali promoted solids, this band shifts progressively from 3200 cm^{-1} for Li and Na samples to 3100 cm^{-1} for K, Rb and Cs samples.

This shift indicates that the alkali promoters increase the basic strength of the solid.

Adsorption of pyrrole on the washed K sample does not give the perturbed NH band observed at 3100 cm^{-1} for the original sample, but only a broadening of the 3400 cm^{-1} band towards lower wavenumbers (Fig.2), which is similar to the band of the undoped chromia-alumina. This result shows that the basic sites, removed by washing originate from the superficial chromate phase.

The catalytic results are given in table 1. 4-Methylpentan-2-ol may be dehydrated to give various olefins or dehydrogenated in Methyl-isobutylketone (5,6). By introduction of alkali promoters, dehydrogenation is increased while dehydration decreases, the effect being more and more pronounced going from Li and Na to K, Rb and Cs. The K sample washed by water refinds an activity very similar to that observed with the pure chromia-alumina, suggesting that the dehydrogenation activity is correlated to the presence of basic sites which originate from the superficial chromate layer.

In summary, it was revealed by the present study that the alkaline ions increase the basic strength of the surface centers while eliminating the Lewis acidity. This modification is connected to an increase in the dehydrogenation/dehydration activity ratio. These effects follow the Li, Na, K, Rb, Cs sequence which has already been observed when using these catalysts for the dehydrogenation of isobutane (1,2). Results also confirm the importance of the surface chromate layer in the catalytic and physico-chemical properties of these oxides.

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TABLE 1

Ratio of dehydrogenation/dehydration activities (expressed as the yield in cm^3 reagent min^{-1} g^{-1}) in reaction of 4-Methyl pentan-2-ol at 360°C.

Al_2O_3-Cr_2O_3	0.04
+ 2.5 % Li	0.11
+ 2.5 % Na	0.89
+ 2.5 % K	7.4
+ 2.5 % Rb	6.8
+ 2.5 % Cs	12.3
Al_2O_3 - Cr_2O_3 + 2.5 % K washed	0.06

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