# IR evidence of zeolitic hydroxy insertion in amide formation by the Ritter reaction

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**IR spectroscopy reveals the incorporation of $^{18}O$ in the zeolitic network upon hydrolysis of a nitrilium complex by $H_2{}^{18}O$ at room temperature in ZSM-5, thus demonstrating participation of zeolitic oxygen in the reaction.**

During the study of stabilised carbenium ions in zeolitic micropores, we have evidenced a new organic reaction on these catalysts, the Ritter reaction. Coadsorption of an alkene and acetonitrile in H-ZSM-5 leads to the formation of a nitrilium complex, which upon hydrolysis yields a substituted amide, detected by IR spectroscopy (Scheme 1).[1]

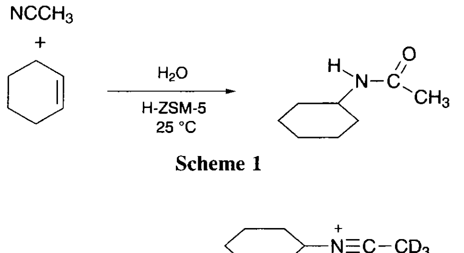
The mechanism originally proposed by Ritter and Minieri remains controversial;[2,3] the intermediate species can be either the ionic nitrilium or a covalent compound with the deprotonated acid used to initiate the reaction.

The nature of the intermediate is still more crucial in zeolites, where carbenium intermediates in acid-catalysed reactions is an important issue. Several authors have reported stable carbenium species,[4,5] while others claimed that these can only be transient carbenium species, stabilised in the form of alkoxy species on the zeolitic network, the cation having no measurable lifetime.[6–9]

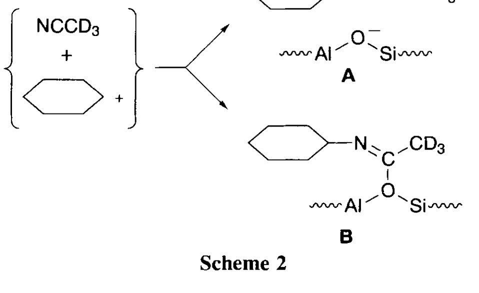
The two postulated intermediate species are shown in Scheme 2: an ionic pair between the nitrilium ion and the deprotonated zeolite (**A**), and a compound with a covalent bond between the carbon atom of the nitrilium and the zeolitic oxygen (**B**).

In order to clarify the nature of the intermediate species, we performed hydrolysis using $H_2{}^{18}O$, and monitored the isotopic variations in the products.

The activated H-ZSM-5 zeolite (Si/Al = 29, Conteka) was first saturated with $CD_3CN$ in an IR cell. Cyclohexene was then introduced at room temperature, protonated by the zeolite, then reacted with acetonitrile to give *N*-cyclohexylacetonitrilium. Excess cyclohexene was removed by vacuum pumping. Hydrolysis was then performed by introducing a few Torr of water vapour at equilibrium. IR spectra were recorded at room temperature with a Nicolet Magna 750 spectrometer (Fig. 1).



**Scheme 1**



**Scheme 2**

The IR spectrum of the activated zeolite [Fig. 1(*a*)] shows two ν(OH) bands in the 3800–3600 cm$^{-1}$ wavenumber range; the 3741 cm$^{-1}$ band corresponds to silanol groups and that at 3604 cm$^{-1}$ to acidic framework SiOHAl groups. After chemisorption of $CD_3CN$ [Fig. 1(*b*)], the silanol ν(OH) band is mostly unaffected whereas the framework hydroxy band disappears. The interaction between the perturbed SiOHAl groups and $CD_3CN$ gives rise to a sharp and strong ν(C≡N) band at 2297 cm$^{-1}$ and to two broad bands at 2800 and 2400 cm$^{-1}$, characteristic of a strong hydrogen bond. Full attribution of the spectrum has been given in a previous paper.[4] Introduction of cyclohexene into the sample after acetonitrile adsorption [Fig. 1(*c*)] leads to many bands in the range 3100–2800 cm$^{-1}$ due to cyclohexene chemisorbed species. The important point is the appearance of a band at 2385 cm$^{-1}$ at the expense of those previously attributed to acidic OH and to hydrogen-bonded acetonitrile. The band at 2385 cm$^{-1}$ has been assigned to the ν(C≡N) vibration of a nitrilium ion (carbenium + acetonitrile),

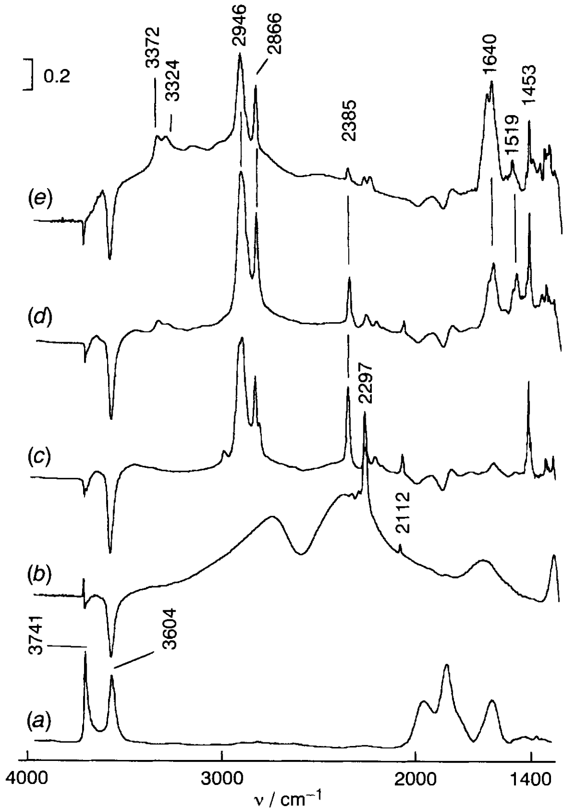


**Fig. 1** IR spectra of the activated zeolite (*a*), after saturation with $CD_3CN$ (*b*), after subsequent addition of cyclohexene (*c*), and hydrolysis with $H_2{}^{16}O$ (*d*) or $H_2{}^{18}O$ (*e*). Spectra (*b*)–(*e*) are obtained after subtraction of spectrum (*a*).

and we have shown that the nature of the carbenium could be determined by the exact position of this band.[4]

Hydrolysis proceeds at room temperature in a few tens of minutes. The obtained IR spectrum shows the formation of a secondary amide [Fig. 1(*d*)] by the Ritter reaction. The bands at 3372 and 3324 cm$^{-1}$ correspond to ν(NH) vibrations of a secondary amide and the bands between 2950 and 2860 cm$^{-1}$ correspond to the ν(CH) vibrations of the cyclohexyl group. The band at 2385 cm$^{-1}$ arises from CN vibration of unreacted nitrilium. The band at 1640 cm$^{-1}$ corresponds to an amide I band [ν(CO)] and that at 1519 cm$^{-1}$ corresponds well to the amide II [ν(CN), δ(NH)] of a secondary amide.

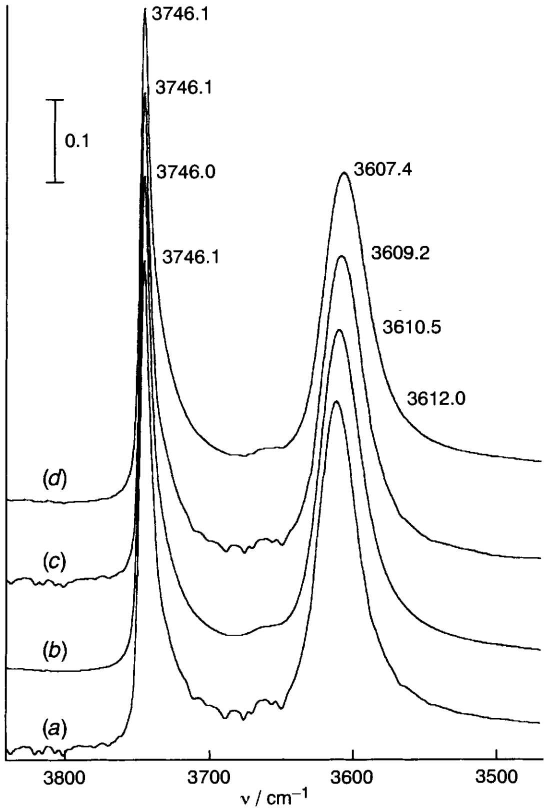
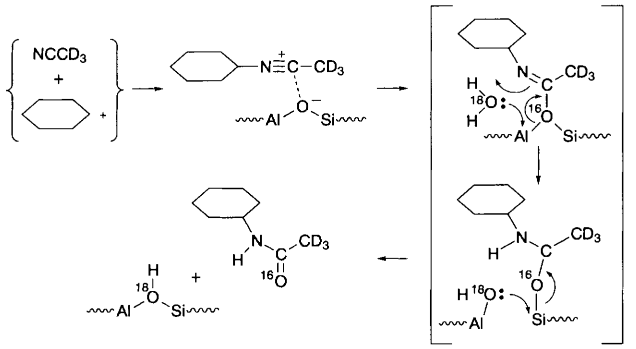


**Fig. 2** IR spectra of the activated zeolite (*a*) and after successive Ritter reactions with $H_2{}^{18}O$ [(*b*)–(*d*)]



**Scheme 3**

IR spectroscopy is a technique particularly well suited to observe isotopic variations and the replacement of $^{16}O$ by $^{18}O$ corresponds to a shift towards lower wavenumbers for the ν(OH) and for ν(C=O) vibrations (12 and 25 cm$^{-1}$, respectively).[10,11] Upon hydrolysis by $H_2{}^{18}O$ [Fig. 1(*e*)], the amide obtained did not show the typical shift of an amide I band upon isotopic change, while the zeolite obtained by desorption of the amide contained $^{18}O$ in the acid hydroxy groups. Reproducing the reaction several times on the same zeolite sample progressively increases the amount of $^{18}O$ introduced (Fig. 2).

We checked that in the absence of acetonitrile and cyclohexene, the zeolite did not incorporate any $^{18}O$ when, after adsorption of $H_2{}^{18}O$ at room temperature, it is reactivated under the same conditions as when desorbing the amide.

The non-acidic silanol hydroxy groups are not exchanged by hydrolysis of the nitrilium ion, while they are more easily exchanged by heating in the presence of $H_2{}^{18}O$.[12] This demonstrates that during the hydrolysis, the zeolitic oxygen is strongly bound to the nitrilium ion, and that it leaves the zeolite to form the amide while oxygen from water replaces the leaving oxygen in the framework of the zeolite.

Since the triple bond is clearly visible in the IR spectrum, we can state that the intermediate species of the reaction is a nitrilium ion, which is strongly bound to the zeolitic oxygen atom *via* a carbon atom, and evolves into a transient alkoxy species during hydrolysis (Scheme 3).

In conclusion, we can state that IR spectroscopy is especially suited for the study of the participation of zeolitic framework oxygen in reactions, by the use of isotopes, and that hydrolysis of nitrilium ions in ZSM-5 proceeds *via* a transient alkoxy species.

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