



Carbonylation of dimethyl ether in mordenite using Inelastic Neutron Scattering

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ABSTRACT

Zeolite mordenite (MOR, Si/Al = 10) was used as catalyst for the reaction between CO and dimethyl ether (DME) to give methyl acetate. Since the reaction is catalysed by Brønsted acid sites, Inelastic Neutron Scattering (INS) is an appropriate technique to identify the intermediates. Although the accepted mechanism goes through an adsorbed methoxy, its characteristic peak at 963 cm^{-1} was only detected in the reaction MOR + DME, in the absence of CO. When CO is present, the peak at 963 cm^{-1} is substituted by other peaks that give valuable information of the reaction intermediates, indicating that either methoxy intermediates are not formed or are quickly replaced by the acetyl intermediate, $[\text{SiO}(\text{COCH}_3)\text{Al}]$, strongly stabilised in the micropore pockets of mordenite. Upon reaction of MOR + CO + DME, a characteristic peak at 1050 cm^{-1} , although being present in liquid methyl acetate, could not be assigned to adsorbed methyl acetate since it loses intensity as the reaction proceeds (upon heating), and was assigned to a strong interaction between CO and DME adsorbed in one or two Brønsted sites, leading to some intermediate that shares this vibrational feature with methyl acetate in liquid phase. Finally, a peak at 1275 cm^{-1} in the spectrum of MOR + CO + DME upon heating is assigned to the formation of methyl acetate when the sample is heated, corresponding to C–O stretching of methyl acetate. This is further confirmed by the absence of this peak before heating. Overall, INS technique has allowed an accurate determination and interpretation of peaks involved in the carbonylation of DME in mordenite.

1. Introduction

Carbonylation of dimethyl ether (DME) with CO for the production of methyl acetate (see equation (6) below) is an industrially relevant catalytic process [1] using zeolites. Certain zeolite topologies have shown a better production of methyl acetate and in particular those that exhibit the carbonylation within their eight-membered rings, notably mordenite and ferrierite [2]. Mordenite (MOR) is the zeolite giving the highest activity for this reaction, containing 12-rings ($6.5 \times 7.0\text{ \AA}$) along [001] and 8-ring side pockets ($3.4 \times 4.8\text{ \AA}$) along [010]. It is well known that the diffusion is another important factor to manipulate the catalytic process, especially for the reactions occurring inside the zeolite micropores due to their confined channels at the nano-scale level [3]. Precisely this is the reason that explains the large activity of mordenite in the carbonylation of DME. The 8-ring side pockets host the reactive sites which are able to reduce the activation barrier through a constrained environment providing an excellent fit for the reactant molecules [4]. On the other hand, the 12-ring channels provide the appropriate

micropores allowing a fast mass transport for both reactants and products [5].

The proposed mechanism is the interaction of DME with Brønsted acid site on zeolites to generate an adsorbed methoxy intermediate, followed by CO insertion giving an acetyl group, which reacts with another DME to produce methyl acetate while regenerating the adsorbed methoxy [6–9], although other mechanisms have been proposed [10,11].

In previous work of carbonylation of DME with CO in mordenite, several relevant bands have been characterised through IR spectroscopy. A band corresponding to adsorbed water appears at 1630 cm^{-1} , and a band at 1458 cm^{-1} from the CH deformation vibration of DME, and two bands at 1496 and 1387 cm^{-1} were associated with COO groups (acetate) [12].

However, there are suggestions that the proposed mechanism may show some inconsistencies. The Gibbs free energy analysis of the formation of methyl acetate from acetyl in the 8-ring pockets of mordenite indicates a large entropic penalty, in contradiction with the

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interpretation of the available experimental data that seems to indicate the 8-ring pockets as the main site of the reaction [4,13]. A computational study [9] indicates a lower barrier when acetyl reacts with methanol, with water also playing an important role, but this can not be claimed when the reactant is DME. Other interpretations of the experimental data have also been proposed [14].

2. Experimental

In this study we propose the combination of Inelastic Neutron Scattering (INS) experiments and Density Functional Calculations (DFT) calculations that may help to provide new results in order to clarify mechanistic aspects of this reaction. Among vibrational spectroscopies, INS presents very appropriate features for our task. This technique is mainly sensitive to vibrations involving hydrogen atoms because of their much higher incoherent cross section (σ_{inc}) compared to other elements. As a consequence, INS is well suited for investigating carbonylation reaction in zeolites, as DME, methyl acetate and methoxy group vibrations can be observed on a wide spectral range, even in regions where signals from the framework atoms would dominate the spectra in other vibrational techniques, for instance, IR or Raman spectroscopy. This would allow us to overcome the interpretation of the complex spectra of IR spectroscopy.

For instance INS has been used to compare the fingerprints of adsorbed methanol in H-zeolites such as H-ZSM-5 and H-Y [15]. The results show that the initial peaks due to Brønsted OH deformations in H-ZSM-5 and H-Y at 1095 cm^{-1} are replaced, after reaction with methanol at room temperature, by the CH bend (X-C-H) and CH_3 rocking mode calculated at 1428 and 1126 cm^{-1} respectively, due to adsorbed methoxy groups. The proposed mechanism to form adsorbed methoxy from methanol produces one water molecule per Brønsted site, whilst when using DME as reactant only one water molecule is produced for two Brønsted sites, hence half of the water amount. A more recent INS study, including the carbonylation of DME shows a very complex spectrum with some of the bands not yet assigned but showing the ability of INS to probe a working catalyst. A pair of bands at 1370 and 1450 cm^{-1} were assigned to symmetric and asymmetric CH_3 bending modes, while CH_3 rocking modes and aromatic CH out of plane bending modes were assigned between 860 and 1050 cm^{-1} [16].

Our study includes INS spectra measured at low T of four samples of DME and DME + CO, both prepared ex-situ at 298 and 498 K (heating), with all samples containing H-mordenite. Other three samples have been also measured for the sake of comparison: H-mordenite, H-mordenite + CO, and H-mordenite + methyl-acetate. Further, periodic DFT calculations of relevant intermediates have been performed, which may help with the assignment of the peaks in the INS spectra.

3. Results

Fig. 1 shows all the seven INS spectra at 10 K measured on IN1-Lagrange in this study corresponding to: H-mordenite (MOR), H-mordenite + CO (MOR + CO), H-mordenite + DME at ambient temperature and heated at 473 K during 2 h (MOR + DME and MOR + DME + heat respectively), H-mordenite + CO + DME at ambient temperature and heated at 473 K (MOR + CO + DME and MOR + CO + DME + heat respectively) and H-mordenite + methyl-acetate (MOR + methyl-acetate) [17,18]. For comparison, the INS spectra of DME and methyl acetate were measured as reference samples. Fig. 1 highlights the relevant peaks that are discussed below (Table 1), indicating the conclusions from the comparison between different spectra.

3.1. H-mordenite (MOR)

The spectrum shows two vibrational bands that are characteristic of the acid sites in zeolites: a broad band below 600 cm^{-1} and a peak at ca. 1080 cm^{-1} that corresponds to the out-of plane and in-plane bending of

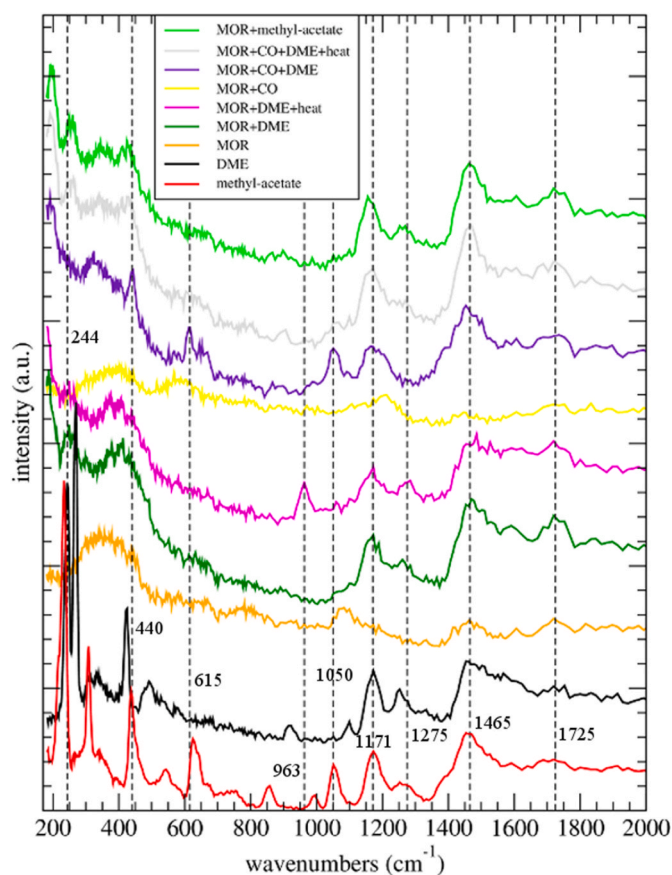


Fig. 1. INS spectra from the samples studied: H-mordenite (MOR), H-mordenite + CO (MOR + CO), H-mordenite + DME with (498 K) and without (298 K) heating (MOR + DME + heat and MOR + DME), H-mordenite + CO + DME with (498 K) and without (298 K) heating (MOR + CO + DME + heat and MOR + CO + DME), and H-mordenite + methyl-acetate (MOR + methyl-acetate). Relevant peaks discussed in the text and assigned in Table 1 are highlighted.

the Brønsted site, respectively. This peak disappears or decreases in intensity in all other spectra, when reactants and intermediates become adsorbed on Brønsted sites. With 48 T-sites per unit cell, a mordenite with $\text{Si}/\text{Al} = 10$ contains ca. $\text{Si}/\text{Al} = 44/4$, 4 Brønsted sites per unit cell. Hence, this peak should disappear completely at reactant/intermediates concentrations larger than 4 molecules/u.c.

3.2. H-mordenite with DME

When DME is adsorbed in H-mordenite without heating (MOR + DME) we observe strong peaks at 1171 and 1465 cm^{-1} assigned to rocking CH_3 and bending CH_3 , respectively. The band appearing at 1465 cm^{-1} appears as a band that contains the doublet of symmetric and antisymmetric bending CH_3 , but with the instrumental resolution it was not possible to separate [16]. At low energies the spectrum shows a broad contribution that corresponds to the out-of plane zeolitic acid sites and a small contribution at $\sim 244\text{ cm}^{-1}$ that corresponds to the vibrational band of torsion CH_3 of the DME [19,20]. A small contribution appears as well at 1080 cm^{-1} that corresponds to the in-plane bending modes of the zeolitic acid sites without adsorbed DME (there is 1 DME/u.c. and 4 Brønsted sites/u.c., with 1 u.c. being 48 T-atoms). These two vibrational bands that correspond to CH_3 appear in all spectra containing DME or methyl acetate.

When heating (MOR + DME + heat), a very clear difference appears and it is the peak at 963 cm^{-1} which we assign to adsorbed methoxy (riding mode CH_3 of the C–O stretching), that should be formed according to the standard accepted mechanism of reaction between DME

Table 1

INS peak assignments from the spectra in Fig. 1 corresponding to the samples studied: H-mordenite (MOR), H-mordenite + CO (MOR + CO), H-mordenite + DME with (498 K) and without (298 K) heating (MOR + DME + heat and MOR + DME), H-mordenite + CO + DME with (498 K) and without (298 K) heating (MOR + CO + DME + heat and MOR + CO + DME), and H-mordenite + methylacetate (MOR + methylacetate). INS peaks from DME obtained from tables of molecular vibrations have also been included [20]. Peak strength: W = weak, S = strong, SS = very strong.

Peak (cm ⁻¹)	Strength	Present in	Assignment
244	SS	DME	Torsions of adsorbed DME.
	S	MOR + DME	
	S	MOR + DME + heat	
	S	MOR + CO + DME	
420, 440	SS	DME	CCO bending of methyl acetate (440 cm ⁻¹) and COC deformation of DME (420 cm ⁻¹). Peak at 440 cm ⁻¹ also present in MOR + CO, assigned to a common feature with acetyl intermediate due to strong zeo-CO interaction.
	SS	MOR + DME	
	SS	MOR + DME + heat	
	SS	MOR + CO + DME	
615	S	MOR + CO + DME	CH ₃ -CO ₂ out-of-plane bending of methyl acetate. Disappears in adsorbed methyl acetate, and present in liquid methyl acetate.
	W	MOR + CO + DME + heat	
963	S	MOR + DME + heat	CO stretching of methoxy.
1050	S	MOR + CO + DME	Peak not from H ₃ C-O stretch of methyl acetate since it loses intensity upon heating. Assigned to acetyl intermediate.
	W	MOR + CO + DME + heat	
1100	S	MOR	In-plane bending Brønsted acid site. Disappears upon adsorption of reactants, intermediates, and products.
1171	SS	DME	Rocking CH ₃ in DME, methoxy and methyl acetate.
	SS	MOR + DME	
	SS	MOR + DME + heat	
	SS	MOR + CO + DME	
	SS	MOR + CO + DME + heat	
1250-1275	S	MOR + DME	Rocking CH ₃ in DME (1250 cm ⁻¹) and C-O stretching in methyl acetate (1275 cm ⁻¹). Does not appear in MOR + CO + DME since methyl acetate is not formed without heating.
	S	MOR + CO + DME + heat	
	W	MOR + CO + DME + heat	
1465	SS	DME	Bending CH ₃ in DME and methyl acetate. Appears in all spectra, even in MOR. Little utility.
	SS	MOR + DME	
	SS	MOR + DME + heat	
	SS	MOR + CO + DME	
	SS	MOR + CO + DME + heat	
	SS	MOR + CO + DME + heat	

and H-mordenite. This result is supported with the calculated frequency of the methoxy group on methanol adsorbed on acid centres of zeolites with DFT calculations [21]. The frequency of the methoxy group was also calculated and measured (at 940 and 1185 cm⁻¹) with DRIFTS [22, 23]. In parallel, the decrease in the intensity of the band at 244 cm⁻¹, associated with DME, further supports that the reaction is taking place.

Also, a peak at 1250 cm⁻¹ appears for MOR + DME that is assigned to

rocking CH₃ of DME. However, MOR + DME + heat shows a band at slightly higher energy, ~1260 cm⁻¹, that is explained by the formation of methyl acetate when the sample is heated, corresponding to C–O stretching as it is shown with Raman spectroscopy in the liquid state [24].

3.3. H-mordenite with DME and CO

A strong peak appears at 1050 cm⁻¹ in MOR + CO + DME which loses intensity upon heating. A peak also at 1050 cm⁻¹ is present in the spectrum of methyl acetate (Fig. 1), corresponding to the H₃C–O stretching (ν_{12}), in agreement with previous results from Raman spectroscopy [24–26], and different from the two O–C stretching peaks in DME that appear at 928 cm⁻¹ and 1102 cm⁻¹, corresponding to symmetric and antisymmetric stretch respectively [19,20]. Hence, ruling out that the peak at 1050 cm⁻¹ in MOR + CO + DME belongs to methyl acetate (see more details in Supplementary data), since it loses intensity upon heating, we assign it as due to a strong interaction between CO and DME adsorbed in one or two Brønsted sites, possibly in the 8-ring pockets of mordenite reported to be very active, leading to some intermediate that shares this vibrational feature with methyl acetate in liquid phase. This is in agreement with the absence of this peak in the spectrum of adsorbed DME (MOR + DME).

Upon heating (MOR + CO + DME + heat) this peak decreases intensity due to the carbonylation reaction that converts the adsorbed CO + DME into methyl acetate (equation (6)). This vibrational band and the ones at 440, 615, 850 and 990 cm⁻¹, that correspond to CCO bending, CH₃–CO₂ out-of-plane bending, H₃C–C stretching and CH₃C rocking on methyl acetate respectively, decrease in intensity when the sample is heated. We therefore hypothesise that an acetyl (or acylium) intermediate, [SiO(COCH₃)Al], is formed (right side of equation (4)) that shares some characteristics with the product (methyl acetate) in liquid phase, namely the vibrations at ca. 440, 615 and 990 cm⁻¹, that appear in the spectrum of MOR + CO + DME (without heating). Importantly, these characteristic peaks of liquid methyl acetate have been reported to disappear when methyl acetate is adsorbed on H-ZSM5 [27], and this is what we observe in the spectra of MOR + CO + DME + heat as well as MOR + methylacetate, in which the peaks at 615, 850, 990 and 1050 cm⁻¹ are not present or show a reduced intensity.

The peak at 1275 cm⁻¹ observed on the reference methyl acetate and the adsorbed MOR + methylacetate corresponds to a C–O stretching (ν_{10}). This vibrational band clearly appears in MOR + CO + DME + heat once the methyl acetate has been formed. However, this peak is not present on the MOR + CO + DME spectrum. This could be explained if we consider that the reaction, before heating, is on the left side of equation (5), with the formed intermediate having a strong interaction between CO and DME.

The presence of specific peaks that are distinctive of the different species involved in the carbonylation of DME makes it difficult to obtain conclusions, but also the absence of certain peaks gives valuable information. We propose two different mechanisms for the early stages of the reaction of DME with Brønsted sites of H-mordenite in the presence and absence of CO.

3.4. In the absence of CO

We propose the accepted mechanism leading to the formation of adsorbed methoxy groups as follows.



With the following overall reaction during the induction period, before C–C bonds are formed:



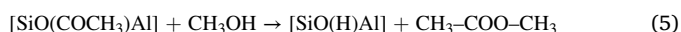
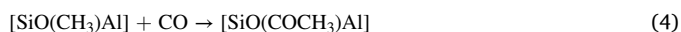
According to this, water should be detected in the spectrum of MOR + DME + heat. However, the absence of the characteristic librational bands of water [28], between 400 and 600 cm^{-1} , on the INS spectrum of MOR + DME + heat suggests that the reaction stops in step (1) and methanol would be hydrogen bonded to the zeolite Brønsted site. A recent study on the interaction of methanol with ZSM-5 has shown the complexity of the INS spectrum [29] and several scenarios are proposed to explain that the bands from Brønsted sites are not observed.

We suggest the key fingerprint is the peak at 963 cm^{-1} , due to adsorbed methoxy, appearing in MOR + DME + heat but not in MOR + DME; whilst the peaks at 1171 and 1465 cm^{-1} , corresponding to the rocking and bending CH_3 , could be due to the methoxy group, or to excess DME. These two peaks, which appear in all spectra since they appear in all CH_3 groups, do not offer relevant information regarding the mechanism.

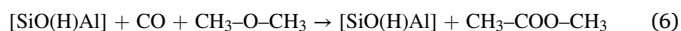
3.5. In the presence of CO

The peak at 963 cm^{-1} , that we assume corresponds to the methoxy formation, does not appear. Its absence in the spectrum of MOR + CO + DME + heat suggests that the DME carbonylation reaction does not go through methoxy intermediate, or either that methoxy intermediate is quickly replaced by the acetyl intermediate, $[\text{SiO}(\text{COCH}_3)\text{Al}]$, strongly stabilised in the micropore pockets of mordenite.

Hence, we propose the mechanism below,

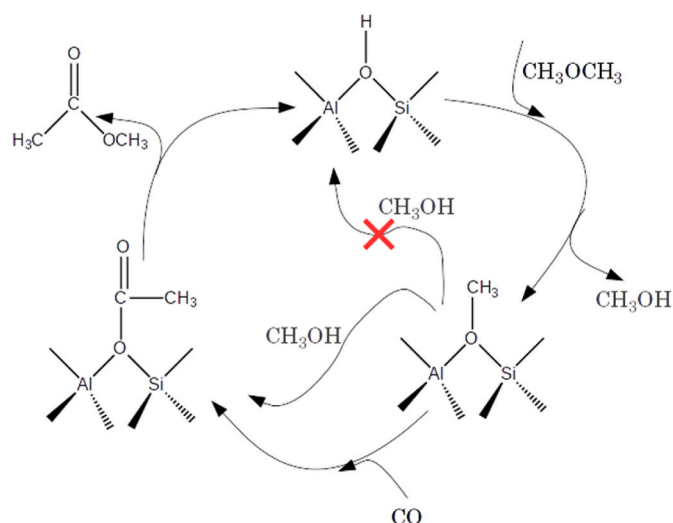


With the overall reaction shown in equation (6) and Scheme 1:



According to this mechanism, Brønsted sites are recovered after the reaction. This has been confirmed when comparing the spectra MOR + CO + DME + heat, MOR + methyl-acetate and MOR (Fig. 1), showing a small contribution on MOR + CO + DME + heat at 1100 cm^{-1} that corresponds to the in-plane bending modes of zeolite Brønsted sites.

The formation of methoxy species is well established in the absence of CO from DRIFT experiments [22,23] which assign the peak at 940 cm^{-1} to C–O methoxy stretching, that we observe at 963 cm^{-1} . In a similar INS study of DME conversion (in H-ZSM-5), Zachariou et al. [16] observed a peak at 958 cm^{-1} , but it was not assigned since the study was mainly focused on the characterization of the coke deposits in working catalysts. The formation and stability of methoxy species formed from DME is also reported from DFT calculations [30], showing a free energy barrier of ca. 130 kJ/mol in H-ZSM-5 from DME at low loading, and ca. 146 kJ/mol at larger loading, with the increase mainly due to entropic effects. A recent in-situ DRIFT study of DME carbonylation on H-mordenite [31] shows the direct observation of acetyl formed by reaction of CO with methoxy at 473 K. The formation rate of acetyl (only observed if the reaction is carried out between 400 and 513 K) was slower than that of methoxy, and also slower than the following acetyl reaction with DME. Bands at 2978 and 2868 cm^{-1} were assigned to the asymmetric and symmetric stretching modes of CH_3 in methoxy, formed by reaction of DME and Brønsted acid sites. A band at 1704 cm^{-1} , was ascribed to the C–O stretch of the acetyl intermediate, but changed immediately after DME was added to the sample with acetyl, with new bands appearing at 1776 and 1758 cm^{-1} , ascribed to the CO stretching in gaseous methyl acetate. The study reports that acetyl intermediate is only formed at CO pressure higher than 0.5 MPa, and below such pressure only polyolefins, with a prominent band at 1600 cm^{-1} , are observed due to the reaction of DME with methoxy species at 473 K.



Scheme 1. Proposed reaction mechanism for carbonylation of DME in mordenite according to INS results.

4. Conclusions

This study has benefited from the main advantages of INS over other spectroscopic techniques for the characterisation of the steps of DME conversion. This method accesses the full energy range and since there are no selection rules, all vibrational modes can be measured. In addition, INS is spatially sensitive to hydrogen atoms and therefore the above mentioned reaction was followed and described step by step.

The analysis of INS spectra of different samples regarding the carbonylation of DME in H-mordenite seems compatible with a reaction leading to methyl acetate without necessarily going through a methoxy intermediate. The methoxy intermediate, that we associate with a peak at 963 cm^{-1} only appears when DME is reacted in H-mordenite in the absence of CO. When CO + DME are reacted, an acetyl (or acylium) intermediate with a distinctive peak at 1050 cm^{-1} , as well as peaks at 440, 615, 850 and 990 cm^{-1} , not present when only DME is reacted and also observed in the spectrum of MOR + CO, seems to indicate that CO is strongly interacting with DME, leading to the acetyl (or acylium) intermediate, $[\text{SiO}(\text{COCH}_3)\text{Al}]$.

Another characteristic peak, at 1275 cm^{-1} , is observed in MOR + CO + DME + heat, and it is absent with no heating. This peak is assigned to the reaction giving methyl acetate, as confirmed by its presence also in the spectrum of adsorbed methyl acetate.

Overall, INS spectra of selected reactants before and/or after heating are able to give sufficient information so as to characterise the species involved in the diethyl ether carbonylation in mordenite.

CRedit authorship contribution statement

Mónica Jiménez-Ruiz: Writing – review & editing, Writing – original draft, Validation, Supervision, Software, Resources, Methodology, Investigation, Formal analysis, Data curation. **Tetiana Lemishko:** Methodology, Investigation, Data curation. **Fernando Rey:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization. **German Sastre:** Writing – review & editing, Writing – original draft, Software, Methodology, Investigation, Formal analysis, Data curation.

Declaration of competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.micromeso.2023.112850>.

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