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Comparison of acid catalysts for the dehydration of methanol to dimethyl ether

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Abstract

The aim of this work is to compare the performance of three acid functions in the dehydration of methanol to dimethyl ether (DME): a) γ-Al_2O_3, b) NaHZSM-5, obtained from NaZSM-5 zeolite subsequent to partial ion exchange with NH_4Cl, and c) HZSM-5-AT zeolite, obtained from NH_4-ZSM-5 treated with NaOH. Ion exchange and treatment with NaOH allow for reducing the acidity of the zeolite, in order to favour methanol dehydration and to avoid the production of C_1-C_4 paraffins, which is important at temperatures above 260 ºC. In the 200-275 ºC range, higher DME yields are obtained with the catalysts based on ZSM-5 zeolite than with the γ-Al_2O_3. Above 260 ºC catalyst that has been treated with NaOH performs slightly better than the one obtained by partial ion exchange.

Keywords: dimethyl ether, methanol dehydration, acidic function

1. Introduction

Dimethyl ether (DME) has aroused great interest, as it can be used directly as a diesel fuel for automobiles with a high cetane number, lower NO_x emission, near-zero exhaust production and reduced engine noise compared to traditional diesel fuels (Bo et al., 2006). The pyrolysis of DME, even at temperatures of up to 1600 ºC and under pressures between 0.8 and 2.9 atm, gives way to an insignificant amount of hydrocarbons of high molecular weight, compared to the pyrolysis of the hydrocarbons that make up diesel fuels. The use of this new fuel is a way of promoting the use of diesel engine cars, as these engines are more efficient than those of gasoline for reducing CO_2 emissions (Fei et al., 2006a,b). DME is also a substitute of LPG in areas where there is no petroleum, due to its similar properties.

Catalytic dehydration of methanol over solid-acid catalysts is a suitable process for DME synthesis, which is the first step in the transformation of methanol into

hydrocarbons (MTG process) or olefins (MTO process). Another possibility is the synthesis of DME in one reaction step from syngas over bifunctional catalysts. In this process methanol dehydration is fundamental for shifting the thermodynamic equilibrium of DME synthesis (Ereña et al., 2005a,b). In both processes the selective DME formation is related to active sites of weak and medium acidity.

Commercially, γ-Al$_2$O$_3$ acid function is used to a large extent in the dehydration of methanol to DME. The vapour phase dehydration of methanol involves a large amount of water as a by-product. Both methanol and water compete with each other for the Lewis acid sites on γ-Al$_2$O$_3$ (Jun et al., 2003). As water is adsorbed more strongly than methanol on γ-Al$_2$O$_3$, this catalyst loses part of its activity during the reaction. Moreover, γ-Al$_2$O$_3$ catalyst is less active than zeolites such as HZSM-5 due to its lower acidity.

Many researchers reported HZSM-5 to be a suitable catalyst for the dehydration of methanol to DME, as its activity is not affected by water. Water in the reaction medium has even a positive effect on methanol dehydration over HZSM-5, as it regenerates the catalyst by removing carbon deposition, thus limiting deactivation by coke formation (Jun et al., 2003). Nevertheless, this catalyst has the inconvenience of the production of hydrocarbons at temperatures above 270 ºC over strong acid sites. In order to avoid the formation of hydrocarbons and to increase the selectivity to DME, modified HZSM-5 catalysts with a lower acidity have been proposed (Jiang et al., 2004; Vishwanathan et al., 2004; Aguayo et al., 2005; Kim et al., 2006).

The aim of this paper is to compare the performance of three acid functions in the dehydration of methanol to DME. These acid functions are: γ-Al$_2$O$_3$, NaHZSM-5 (obtained from NaZSM-5 zeolite subsequent to partial ion exchange with NH$_4$Cl) and HZSM-5 zeolite treated with NaOH. Both partial ion exchange and treatment with NaOH allow for obtaining moderate acid sites in the zeolite, which, on the one hand, are active in the dehydration of methanol and, on the other, are of low activity in the formation of hydrocarbons and olefins.

2. Experimental

The γ-Al$_2$O$_3$ acidic function has been prepared following the method of coprecipitation of a NaAlO$_2$ suspension with 2M solution of HCl at 70 ºC, until pH reaches a value of 8.5, Figure 1 (Li et al., 1996; Garoña 2006). The subsequent steps are the aging of the catalyst at 70 ºC during 1 h, filtering, washing, drying (at 25 ºC and at 110 ºC during 12 h each) and calcination (550 ºC, 2 h).

The NaHZSM-5 acidic function, Figure 2, has been obtained from NaZSM-5, after partial elimination of Na$^+$ cation by ion exchange with 1 M solution of NH$_4$Cl and calcination at 550 ºC during 2 h (Garoña, 2006).

The third catalyst has been obtained from NH$_4$-ZSM-5 zeolite treated with a 0.2 M solution of NaOH during 5 h. The sodic zeolite (NaZSM-5) is cooled, filtered, dried

and, subsequently, undergoes ion exchange with a 1 M solution of NH_4NO_3 at 550 °C during 2 h. The last step in the preparation of the active phase HZSM-5-AT is the calcination. Figure 3 shows a block diagram of the steps followed in the preparation of the zeolite treated with alkali, HZSM-5-AT.
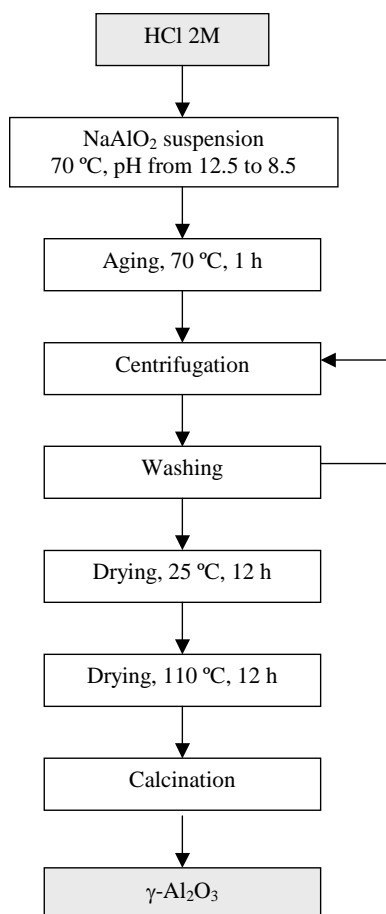

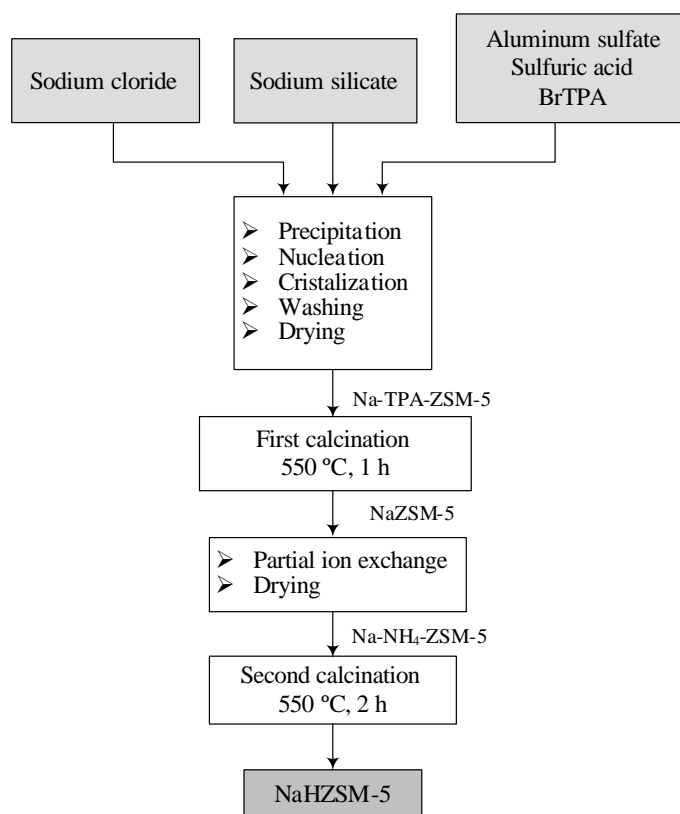Figure 1. Preparation steps of the γ-Al_2O_3 acidic function.

Figure 2. Preparation steps of the NaHZSM-5 acidic function.

The acid strength distribution of the catalysts has been calculated from the data of the differential heat of adsorption of NH_3 and the mass adsorbed during this process (Aguayo et al., 1993, 1994). Runs have been performed in a TG-DSC111 calorimeter, which measures simultaneously heat flow and the thermogravimetric signal (TGA). NH_3 adsorption has been carried out at 150 °C after sweeping with helium at 350 °C in order to remove the impurities on the catalyst surface.

The acid strength distribution of the three catalysts (γ-Al_2O_3, NaHZSM-5 and HZSM-5-AT) is shown in Figure 4. The total acidity of γ-Al_2O_3 (0.045 mmol NH_3 g^{-1}), is one order of magnitude lower than that of NaHZSM-5 (0.54 mmol NH_3 g^{-1}) and HZSM-5-

AT (0.51 mmol NH_3 g^{-1}). Nevertheless, these values of acidity of zeolite-based catalysts are low enough to reduce the proportion of light olefins and improve the DME yield in the reactor outlet stream (Vishwanathan et al., 2004).
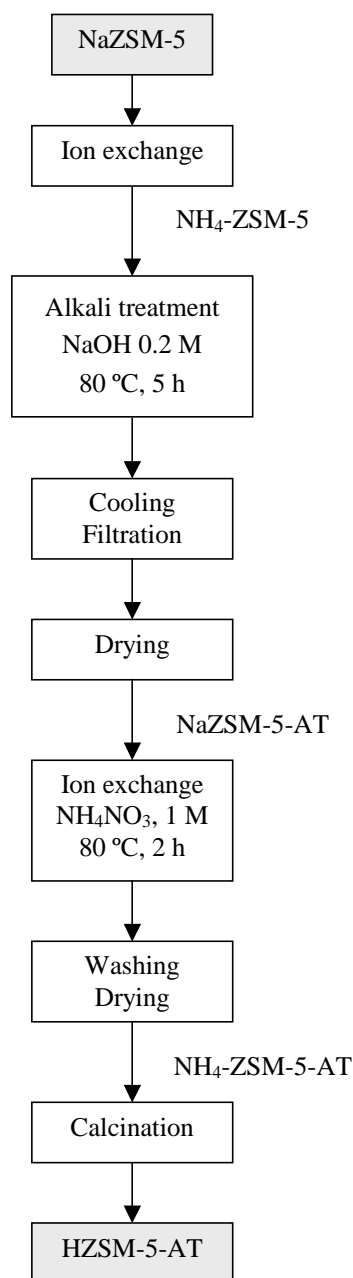
On the other hand, the acidic strength of HZSM-5-AT (90 kJ/mol NH_3) is slightly lower than that of the partially sodic zeolite NaHZSM-5 (110 kJ/mol NH_3). This result is indicative of the effectiveness of the alkaline treatment with NaOH (5 h of duration) for obtaining a zeolite with a suitable acid strength distribution to carry out the methanol dehydration reaction.
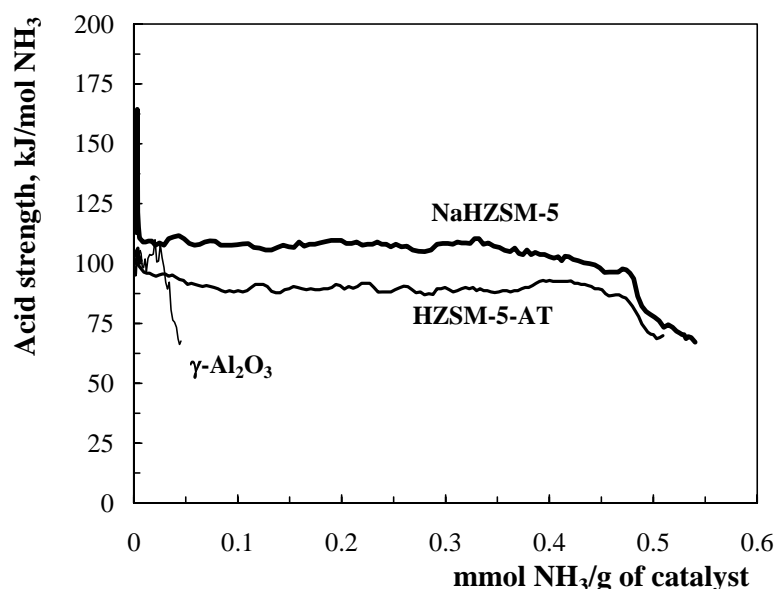
```
       NaZSM-5
          │
          ▼
     Ion exchange
          │
       NH₄-ZSM-5
          │
          ▼
    Alkali treatment
      NaOH 0.2 M
      80 ℃, 5 h
          │
          ▼
       Cooling
      Filtration
          │
          ▼
       Drying
          │
       NaZSM-5-AT
          │
          ▼
    Ion exchange
     NH₄NO₃, 1 M
      80 ℃, 2 h
          │
          ▼
       Washing
       Drying
          │
      NH₄-ZSM-5-AT
          │
          ▼
     Calcination
          │
          ▼
      HZSM-5-AT
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Figure 4. Results of differential adsorption calorimetry of NH_3 at 150 ℃, for γ-Al_2O_3 and the catalysts based on ZSM-5 zeolite.

Figure 3. Preparation steps of the HZSM-5-AT acidic function.

The reaction equipment used, PID Eng. & Tech. Microactivity-Reference, is provided with a fixed bed and allows for operating at high temperatures and pressures, Figure 5. The on-line analysis of reaction products has been carried out by means of a Varian CP-4900 gas micro-chromatograph. The following operating conditions have been used: temperature, in the 200-275 ºC range; pressure, 15 bar; space time, 5.6 (g of catalyst) h (mol of methanol)$^{-1}$.
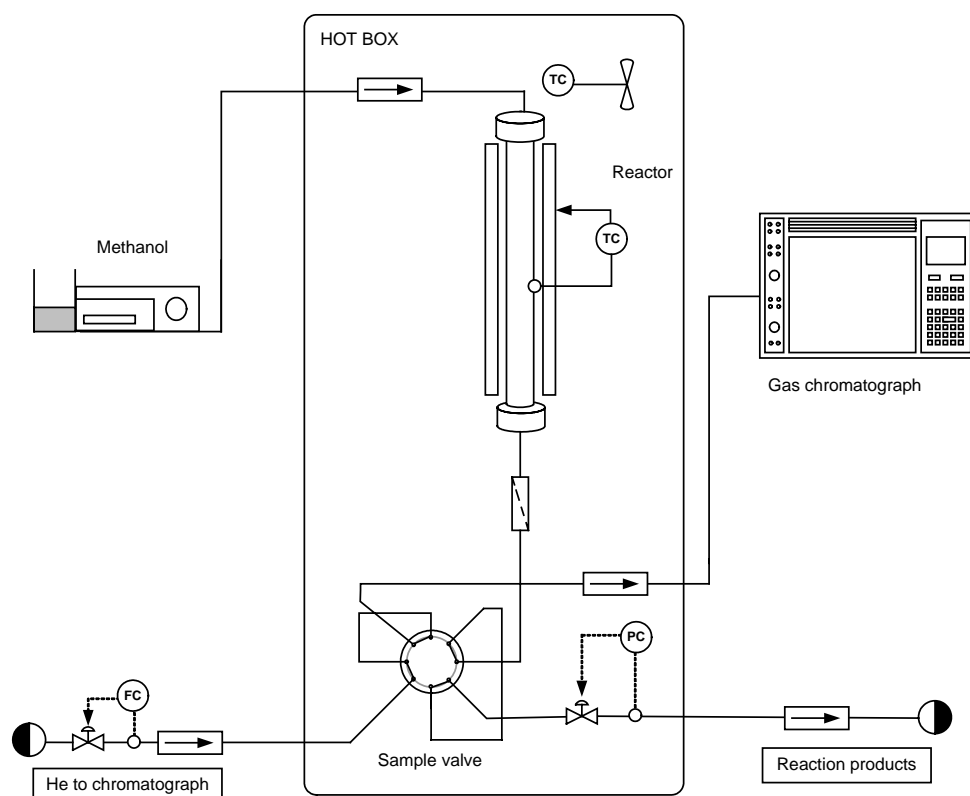
Figure 5. Experimental equipment used in the dehydration of methanol to DME.

3. Results and discussion

Methanol conversion (X) has been calculated as the percentage of carbon atoms fed in the methanol that converts to organic compounds (hydrocarbons, DME and olefins):

$$X = \frac{(n_{C_S})_{HC} + 2n_{DME} + (n_{C_S})_{olefins}}{(n_{MeOH})_0} 100 \tag{1}$$

where n_{DME} is the molar flowrate of DME in the reactor outlet stream, $(n_{CS})_{HC}$ and $(n_{CS})_{olefins}$ are the molar flowrates, in carbon basis, of hydrocarbons and olefins, respectively, and $(n_{MeOH})_0$ is the molar flowrate of methanol in the feed.

DME yield (Y_{DME}) has been determined as the percentage of carbon atoms fed which converts to DME:

$$Y_{DME} = \frac{2n_{DME}}{(n_{MeOH})_0} 100 \qquad (2)$$

The yields of by-products ($Y_{olefins}$ and Y_{HC}) have been defined as the percentage of carbon atoms fed in the form of methanol that converts to olefins and hydrocarbons:

$$Y_{olefins} = \frac{(n_{C_S})_{olefins}}{(n_{MeOH})_0} 100 \qquad (3)$$

$$Y_{HC} = \frac{(n_{C_S})_{HC}}{(n_{MeOH})_0} 100 \qquad (4)$$

Figure 6 shows the effect of temperature on the conversion of methanol for the three acidic functions. The catalysts based on ZSM-5 zeolite, (NaHZSM-5 and HZSM-5-AT) have a much higher activity than γ-Al$_2$O$_3$. This is due to the acid density of the catalysts based on zeolite ZSM-5, which is much higher than that of γ-Al$_2$O$_3$. Moreover, the higher water adsorption capacity on the Lewis acid sites of γ-Al$_2$O$_3$ leads to a lower methanol conversion (Vishwanathan et al., 2004; Ereña et al., 2005b). The catalysts based on zeolite ZSM-5, on the contrary, have a high water resistance due to the hydrophobic properties resulting from the high SiO$_2$/Al$_2$O$_3$ ratio.

Figure 7 shows the evolution of DME yield with temperature for the three acidic catalysts. It is observed that higher DME yields are obtained with the catalysts based on ZSM-5 zeolite than with γ-Al$_2$O$_3$. For NaHZSM-5 and HZSM-5-AT, DME yield is almost the same (between 90 and 94 %) up to temperatures of 260 ºC, and there is a slight difference above this temperature, due to the loss of DME selectivity (methanol conversion is almost the same) for NaHZSM-5 catalyst. The difference between both catalysts at 275 ºC is a consequence of the higher increase in the yields of hydrocarbons and olefins for NaHZSM-5 catalyst, as it is shown in Table 1.

Vishwanathan et al. (2004) reported that the formation of hydrocarbons for NaHZSM-5 catalyst is important at temperatures above 270 ºC, which is in good agreement with the results listed in Table 1. The production of hydrocarbons at temperatures above 260 ºC is greatly reduced when using HZSM-5-AT, probably due to its lower acid strength (Figure 4), which prevents the reaction that produce C$_1$-C$_4$ paraffins. Kim et al. (2006) reported that, for γ-Al$_2$O$_3$ catalyst, the formation of hydrocarbons becomes

to be significant at a much higher temperature (370 ºC), due to its low acidity. The formation of olefins has only been detected for NaHZSM-5 at 275 ºC.
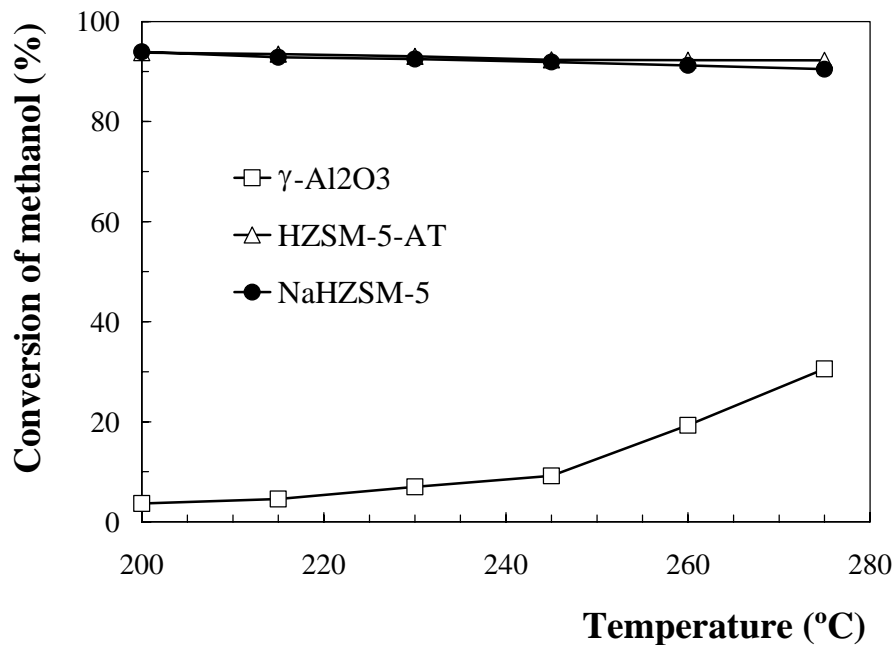

Figure 6. Effect of temperature on methanol conversion for the three acidic catalysts.
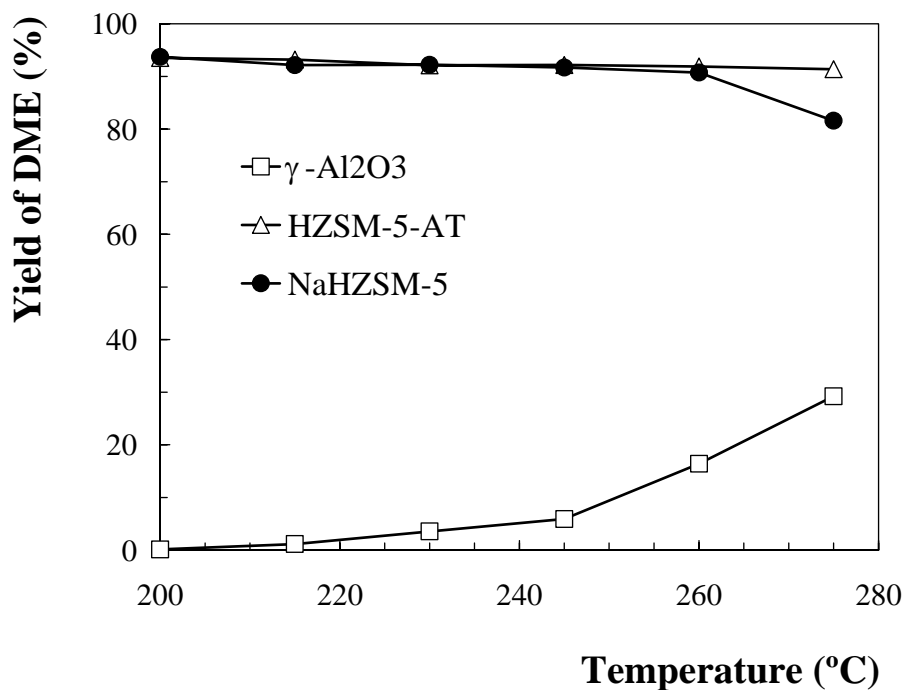

Figure 7. Effect of temperature on DME yield for the three acidic catalysts.

Table 1. Yield of by-products (hydrocarbons and olefins) for the highest temperatures studied, 260 and 275 ºC.

Acidic function	260 ºC		275 ºC	
	HC yield (%)	Olefins yield (%)	HC yield (%)	Olefins yield (%)
γ-Al_2O_3	1.9	---	1.3	---
HZSM-5-AT	0.4	---	0.8	---
NaHZSM-5	0.4	---	7.5	1.5

4. Conclusions

Higher DME yields are obtained with the catalysts based on ZSM-5 zeolite than with the γ-Al_2O_3 acidic function. DME yield is almost the same up to temperatures of 260 ºC, for NaHZSM-5 and HZSM-5 treated with NaOH, and there is a slight difference above this temperature. The more severe treatment with NaOH allows for obtaining a zeolite (HZSM-5-AT) with a more suitable acid strength for avoiding the formation of hydrocarbons and olefins at temperatures above 260 ºC.

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