CO hydrogenation on alumina pre-treated with sodium acetate aqueous solution

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CO hydrogenation was studied over various alumina catalysts, untreated, pre-treated with sodium acetate (NaOAC) and calcined at 773 K after treatment. The catalysts were characterized by means of XRD and IR spectroscopy after pyridine adsorption. An apparent increase of ethylene selectivity over NaOAC pre-treated catalyst was observed. Both CO conversion and ethylene selectivity depended on the temperature of CO hydrogenation and a new γ-Al_2O_3 layer formed by surface boehmite transformation at elevated temperature on the original alumina surface. Several probe molecules, including HCl, NH_3 and pyridine, were used to detect the active sites for CO hydrogenation. There are two kinds of active sites (e.g. Lewis acidic and basic sites) which seem to be involved in the heterolytic dissociation of hydrogen to form a hydroxyl. Thus, the hydroxyl possibly plays a very important role in the formation of formyl, which may be the intermediate of the methoxide, and the methoxide seems to be the intermediate for hydrocarbons.

Keywords: γ-Al_2O_3; sodium acetate; CO hydrogenation; surface boehmite; Lewis acidic and basic sites

1. Introduction

Alumina is widely used as a support for active catalyst phases and also as a catalyst in its own right for reactions including those of dehydration, isotope exchange, isomerization, cracking, alkylation and hydrogenation of alkenes [1–3]. However, it is not renowned for its ability to catalyze the hydrogenation of carbon monoxide. The sites on the surface of Al_2O_3 associated with adsorption and catalysis are generated at temperatures between 623 and 1073 K [1,2]. The surface is dehydroxylated at elevated temperatures to produce Lewis acidic and basis sites:

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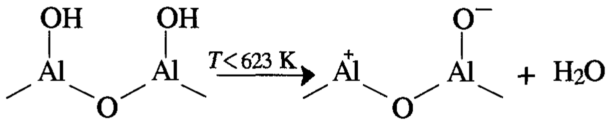


$$\overset{\text{OH}}{\text{Al}}-\text{O}-\overset{\text{OH}}{\text{Al}} \xrightarrow{T<623\ \text{K}} \overset{+}{\text{Al}}-\text{O}-\overset{\text{O}^-}{\text{Al}} + H_2O \qquad (1)$$

Reaction (1) leads us to expect equal numbers of acidic and basic sites on the surface of alumina [4]. Bond et al. [3] found that two types of site might be involved in alkene hydrogenation over γ-Al_2O_3; the first adsorbing hydrogen and initiating spillover to the second type of site, where the alkene was adsorbed and hydrogenated. These might be anionic oxygen and Lewis acid respectively. The results of our laboratory [5] indicate that metal oxides are really good candidates for CO hydrogenation to light olefins. Therefore, the assumption that less amount of olefin is hydrogenated further to paraffin on metal oxides in comparison with metal catalysts seems to be correct. Alumina was selected for this study because it was one of the major components of methanol producing catalysts in industry and had been well studied. Bond et al. found that very active sites for alkene hydrogenation could be generated via sodium acetate pretreatment of γ-Al_2O_3 and were located at the boundary of boehmite and γ-Al_2O_3 phases. Therefore, this study was focused on CO hydrogenation on either NaOAC treated or untreated alumina for comparison. Possible active sites for hydrogen and CO activation were proposed.

2. Experimental

The three aluminas with different boehmite contents used in this study were purchased from Wenzhou Chemicals (China). The total content of metal impurities is less than 50 ppm analyzed by means of ICP atomic emission spectroscopy; neither iron nor other transition metals were detected by XPS. These aluminas are designated by 201, 204, 208. The BET surface areas are 172, 158 and 178 m^2/g respectively. NaOAC pretreatment was carried out as described by Bond et al. [3]. Each 18 g of those aluminas was refluxed with 500 ml of 1 mol/ℓ sodium acetate aqueous solution (prepared from A.R. grade reagent) at 373 K for 16 h. A sample was obtained by filtering and washed thoroughly with 1300 ml of boiling distilled water to remove sodium acetate. The thus obtained samples are designated by AC201, AC204, AC208 respectively. Those samples subjected to calcination at 773 K in air for 1 h are designated by AC201(773), AC204(773), AC208(773). The BET surface area of these samples was scarcely changed by NaOAC treatment.

Catalyst characterization was performed with a Specord 75IR instrument and a Rigaku DMax/RB X-ray diffraction instrument. A quartz IR cell was used for in situ treatment of the sample which was evacuated to 10^{-3} Torr before IR measurement.

The CO hydrogenation reaction was carried out in a stainless steel reactor ($\varnothing 8 \times 300$) with 2.0 ml of catalysts (20–60 mesh). The reaction conditions were

1.0 MPa of syngas (which was purified by passage through a pipe of a mixture of active carbon and basic alumina, $H_2/CO = 2$), 600 h^{-1} of space velocity, at 573, 623, 673, 723 K. An on-line gas chromatograph with an FID and capillary column was utilized for hydrocarbon analysis. A thermal conductivity detector was used for CO and CO_2 analysis. In our experiment less than 0.5% of CO_2 in the outlet gas was produced; it was not counted into CO conversion. CO conversion was calculated by carbon balance, except for carbon dioxide. The selectivity to hydrocarbons was calculated by normalizing all the hydrocarbons produced. More experimental data can be found elsewhere [5].

3. Results and discussion

Fig. 1 is the X-ray diffraction pattern of samples 201, 204 and 208. The peaks at $d = 1.38$ and 2.40 indicate these three samples are all γ-Al_2O_3. It is apparent that the peaks at $d = 6.12$, 3.16 and 2.35 indicate the existence of boehmite in both 204 and 201. The percentage of boehmite in each of them could be estimated by the intensity ratio of $d = 6.12$ to $d = 1.39$. The contents of boehmite in 204, 201, and 208 are about 50%, 5% and 0% (wt) respectively. No X-ray lines attributable to any other phases were observed. Fig. 2 is the X-ray diffraction pattern of AC204, AC204(773), AC208 and AC208(773). Compared to fig. 1, it is true that a small amount of boehmite was formed after NaOAC pretreatment over 208 which is consistent with the results of Bond et al. [3]. For 204, after NaOAC pretreatment, the peaks of boehmite become sharper and narrower, but the content of γ-Al_2O_3 is still high (about 40%). The patterns of AC204(773) and AC208(773) are the same, consisting of the diffraction pattern of γ-Al_2O_3 only: no lines attributable to boehmite

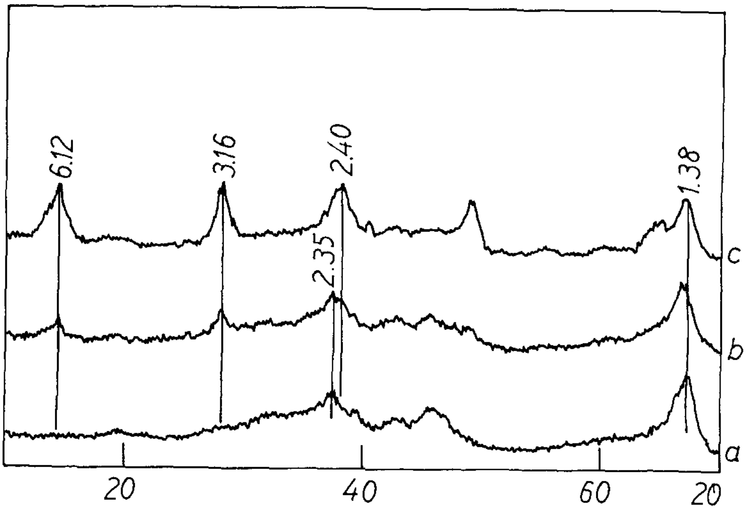


Fig. 1. XRD pattern of alumina. (a) 208, (b) 201, (c) 204.

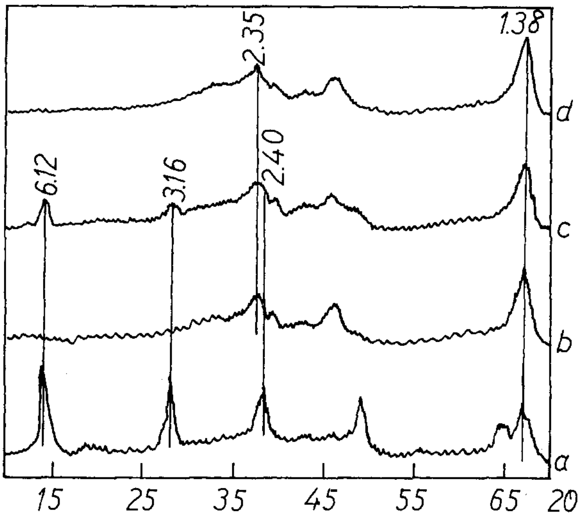


Fig. 2. XRD pattern of alumina. (a) AC204, (b) AC204(773), (c) AC208, (d) AC208(773).

can be detected. These results show that the boehmite phase exists either in the bulk phase of γ-Al_2O_3 (as in the case of 204), or on its surface (as in the case of 208) [3]. It changes to γ-Al_2O_3 after calcination at 773 K.

Tables 1–3 present the results of CO hydrogenation on 201, AC201, 204, AC204, 208 and AC208 at different temperatures under the conditions described above. First, it can be seen that NaOAC pretreatment resulted in an apparent increase of yields of hydrocarbons with two and more carbon numbers (C_{2+}) along with the decrease of methane formation on all of the samples 201, 204 and 208. Second, the olefin to paraffin ratios (expressed by olefin percentage in total olefin and paraffin) on 208 at and above 673 K were increased remarkably after NaOAC pretreatment. However, those ratios for both 204 and 201 which possess boehmite phase, exhibit no apparent changes after NaOAC treatment. Third, the CO conversions on three NaOAC pre-treated samples, as well as on 201 and 204 containing boehmite phase, are less than 1% at and below 673 K, but increase sharply at 723 K. The temperature range at which CO conversions change greatly is almost

Table 1
The data of CO hydrogenation over aluminas termed as 201 and AC201 [a]

T (K)	CO conv. (mol%)	Hydrocarbon selectivity (mol%)				$(C_2^= + C_3^=)/(C_2 + C_3)$
		C_1	C_2	C_3	C_4	
573	0.09(0.09)	97.3(97.5)	2.70(2.50)	0(0)	0(0)	0(0)
623	0.44(0.12)	62.2(91.5)	20.2(6.70)	16.4(1.70)	1.20(0)	0.64(0.77)
673	0.99(0.30)	52.4(71.7)	24.9(18.6)	16.0(9.70)	6.70(0)	0.84(0.83)
723	2.28(1.06)	46.7(59.1)	28.2(25.8)	17.5(12.7)	7.60(2.40)	0.83(0.84)

[a] The data of 201 are listed in parentheses.

Table 2
The data of CO hydrogenation over aluminas termed as 204 and AC204 [a]

T (K)	Co conv. (mol%)	Hydrocarbon selectivity (mol%)				$(C_2^= + C_3^=)/(C_2 + C_3)$
		C_1	C_2	C_3	C_4	
573	0.18(0.09)	97.3(97.0)	2.70(3.00)	0(0)	0(0)	0(0)
623	0.21(0.31)	75.1(68.2)	15.1(16.7)	9.80(13.4)	0(0)	0.78(0.67)
673	0.97(0.83)	62.7(67.7)	20.6(17.9)	11.9(9.80)	4.90(4.60)	0.86(0.85)
723	2.98(1.71)	48.6(51.7)	28.2(25.7)	15.6(13.3)	7.58(9.30)	0.87(0.87)

[a] The data of 204 are listed in parentheses.

the same as that for transformation of boehmite to γ-Al_2O_3 in DTA and TG. XRD patterns showed that lines attributable to the boehmite phase could no longer be detected after CO hydrogenation at 723 K.

Table 4 shows that the sharp change of CO conversions on both AC204(773) and AC208(773) for uncalcined NaOAC pre-treated alumina was not observed. These results indicate a relationship between CO conversion and a newly formed γ-Al_2O_3 layer which perhaps consisted primarily of low coordinated aluminum ions (Lewis acid sites) and oxygen anions (Lewis base sites), which may be formed via dehydroxylation at elevated temperature, as Bond et al. revealed [3]. This suggestion was further supported by the fact that, when the Lewis acidic and basic sites were poisoned by HCl, a sharp decrease of CO conversion was observed, which is analogous to Bond's results. Thus, it is deducible that acidic and basic sites may be active in CO hydrogenation too. The basic sites (oxygen anions) may also be the hydrogen activation sites as in the case of alkene hydrogenation [3], which is in accordance with the effect of ammonia on various metal oxides including alumina [6].

Fig. 3 shows that NaOAC pretreatment affects ethylene selectivity greatly. Such pretreatment resulted in an almost linear increase of ethylene selectivity versus reaction temperature. However, the selectivity to propene is nearly kept constant when the reaction temperature range is at 523 K or higher. Correlating the results of fig. 3 with those of figs. 1 and 2, it is easy to deduce that ethylene selectivity is also affected significantly by the newly formed Lewis acidic and basic sites.

Table 3
The data of CO hydrogenation over aluminas termed as 208 and AC208 [a]

T (K)	CO conv. (mol%)	Hydrocarbon selectivity (mol%)				$(C_2^= + C_3^=)/(C_2 + C_3)$
		C_1	C_2	C_3	C_4	
573	0.11(0.24)	86.7(97.2)	9.20(2.80)	4.10(0)	0(0)	0.61(0)
623	0.19(0.64)	78.2(77.9)	14.8(14.0)	7.00(8.10)	0(0)	0.65(0.60)
673	0.45(1.60)	65.0(68.3)	22.8(17.4)	10.2(9.80)	1.90(4.60)	0.85(0.59)
723	1.99(2.00)	53.8(69.9)	29.5(18.3)	12.5(8.80)	4.20(2.80)	0.89(0.64)

[a] The data of 208 are listed in parentheses.

Table 4
The data of CO hydrogenation over aluminas termed as AC204(773) and AC208(773) [a]

T (K)	CO conv. (mol%)	Hydrocarbon selectivity (mol%)				$(C_2^= + C_3^=)/(C_2 + C_3)$
		C_1	C_2	C_3	C_4	
573	0.20(0.18)	95.2(97.3)	4.80(2.30)	0(0)	0(0)	0.45(0)
623	1.00(0.73)	62.1(67.6)	19.7(17.5)	14.5(13.1)	3.70(2.80)	0.70(0.62)
673	1.61(1.49)	56.1(58.1)	23.5(21.9)	13.3(13.6)	7.10(6.40)	0.85(0.79)
723	3.26(3.68)	48.8(52.1)	31.9(27.0)	14.3(14.2)	4.90(6.70)	0.87(0.82)

[a] The data of AC204(773) are listed in parentheses.

It is interesting that AC208 pre-evacuated at 423 K shows very weak Lewis acidity measured by pyridine adsorption (fig. 4, bands at 1610 and 1445 cm^{-1}), the adsorbed pyridine species could be easily desorbed at 423 K for 10 min evacuation, but those on AC208 pre-evacuated at 573 K and on AC208(773) could not be desorbed at the same temperature with evacuation. These observations reveal that a layer of boehmite which possess very weak Lewis acidity, covers the surface of γ-Al_2O_3, and the Lewis acidic sites can be formed at and above 573 K. If we also assume that equal numbers of acidic and basic sites are formed, their numbers will increase with the increase of reaction temperature on NaOAC pre-treated samples. As Knözinger [3] described, only a small percentage of oxygen anions are active sites, both the number and the percentage of active sites will increase along with the increase of activation temperature (i.e. reaction temperature). Thus the lin-

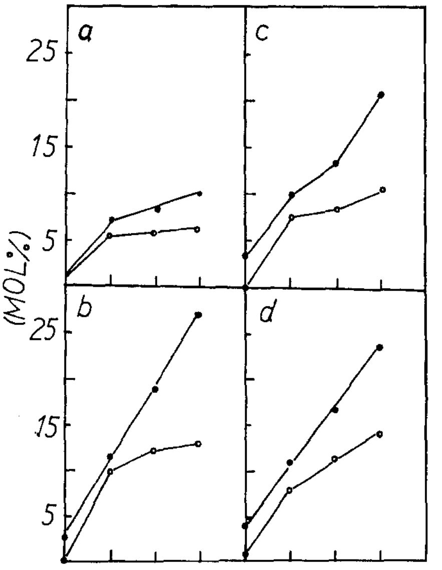


Fig. 3. Ethylene (●) and propene (○) selectivity versus reaction temperature. (a) 208, (b) AC208, (c) 204, (d) AC204.

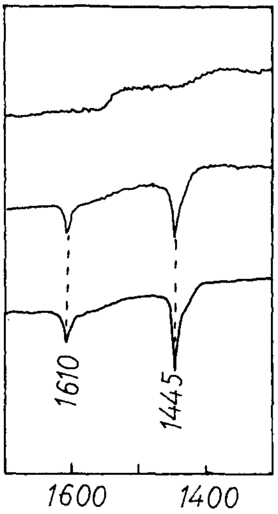


Fig. 4. IR spectra of pyridine adsorbed on alumina pre-evacuated at various temperatures. (a) Py adsorbed on AC208 at 423 K, (b) Py adsorbed on AC208 at 333 K, (c) Py adsorbed on AC208(773) at 423 K.

ear increase of ethylene selectivity versus reaction temperature seems to be related to the newly generated active sites (fig. 3), perhaps to the oxygen anions (i.e. basic sites). The results given in fig. 5 support that the selectivity to ethylene is really related to the percentage of active sites because the total numbers of oxygen anions could not be changed apparently after calcination of NaOAC pre-treated alumina. In addition, only the non-active sites could be changed to active ones during the increase of reaction temperature on AC204(773) and AC208(773). In order to further confirm this proposition, a test of severe hydrogen treatment (at 823 K for 1 h) was carried out on AC208(773). The CO conversion decreased sharply almost to zero. This phenomenon could be explained as follows: in the high temperature hydrogen treatment the valence of Al^{3+} is not changed, however, the oxygen anions on alumina could heterolytically dissociate hydrogen to form hydroxyl [7] which

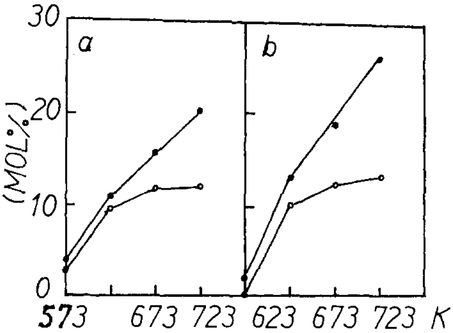
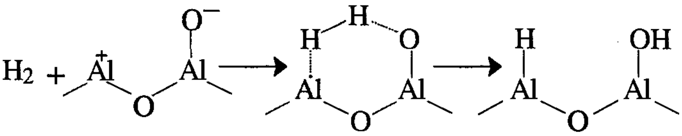


Fig. 5. Ethylene (●) and propene (○) selectivity versus reaction temperature. (a) AC204(773), (b) AC208(773).

could be dehydrated at elevated temperature (e.g. 823 K), thus the number of active oxygen anions would be decreased, which resulted in a decrease in CO conversion and ethylene selectivity.

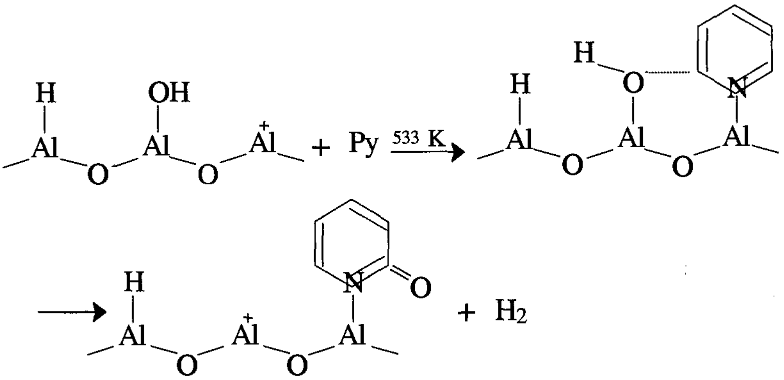
In addition to the above mentioned considerations, one may argue that some metallic impurities such as iron either in alumina or from syngas may play a very important role in CO hydrogenation here instead of coordinatively unsaturated ions. In fact, XPS did not detect any iron and other potentially active metal species. The impurities in all of the used aluminas consisted predominantly of sodium. Its content does not change apparently before and after both NaOAC pretreatment and CO hydrogenation. When AC204(773) was subjected to a helium stream at 723 K which bubbled through a bath of $Fe(CO)_5$ at room temperature for 10 min, its ethylene selectivity decreased sharply although its CO conversion changed slightly. Therefore, it is reasonable to exclude the role of the impurity in CO hydrogenation over the aluminas studied here.

In summary, CO hydrogenation on γ-Al_2O_3 seems to behave like alkene hydrogenation. There are two active sites involved in the activation of CO and H_2 respectively. CO was adsorbed on Lewis acidic sites. This consideration could be supported by Knözinger's [1] and Morterra's [8] results that CO could be held on Lewis acidic sites, characterized by IR spectroscopy. Bond [3] found CO could poison the sites for alkene hydrogenation at lower temperature (e.g. 393 K) on boehmite/γ-Al_2O_3 catalysts. Therefore, it is reasonable that we could not find any CO hydrogenation activity at lower temperatures (e.g. 393, 473 K) on all the NaOAC pre-treated catalysts in this work. In other words, the very active sites located between the phases of boehmite and γ-Al_2O_3 as described by Bond et al. [3] had been completely poisoned by CO in the case of CO hydrogenation. For H_2, it could be activated by heterolytic dissociation on oxygen anions and neighboring metal ions [7]. Although Bond et al. also suggested that hydrogen was activated on oxygen anions, they did not give the model of H_2 dissociation. Both Knözinger [1] and Hall [9] suggested that both basic and acidic sites are involved in hydrogen and alkane heterolytic dissociation. All these results and the study of H_2 adsorption on metal oxides [10–12] forced us to consider that the hydrogen dissociation on oxygen anions must be connected to the neighboring located Lewis acidic sites, which can be schemed as follows:

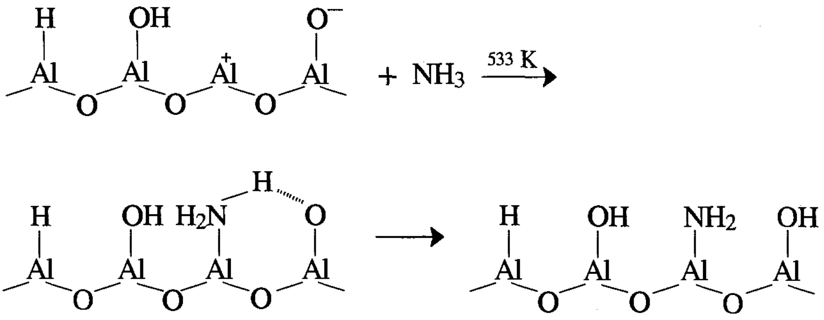


Thus formed, hydroxyl may be bifunctional either as a hydrogen spillover reservoir [3,13] or as a basic hydroxyl attacking adsorbed CO to form formyl [14,15], which can be easily hydrogenated to methoxide species [16,17]. It seems that the second mechanism is more possible for CO hydrogenation. This was supported by a CH_3I

trapping test in which dimethyl ether was obtained on the used metal oxide catalyst for CO hydrogenation [18]. This indicates the existence of intermediate methoxide species on the used catalyst surface. This was also supported by the experiment with alumina completely poisoned by pyridine for CO hydrogenation at 633 K. Pyridine could consume basic hydroxyl at and above 573 K [19,20] according to the following scheme, and some Lewis acidic sites were blocked at the same time:



However, when NH_3 is used instead of pyridine, a promotion of CO hydrogenation over metal oxide catalysts has been observed [6]. It is believed that NH_3 is heterolytically dissociated according to the following scheme:



This suggestion could be supported by the results of an ammonia adsorption study on alumina [21], in which the concentration of active hydroxyl was increased, which may result in a promotion of CO hydrogenation.

4. Conclusion

Based on the results of this work, it is possible to deduce the following conclusions: (1) The boehmite formed on γ-Al_2O_3 via NaOAC aqueous solution pretreatment can be dehydroxylated to a layer of newly formed γ-Al_2O_3 on the original

γ-Al_2O_3 which may consist of active Lewis acidic and basic sites (i.e. surface oxygen anions). (2) Both the acidic and the basic sites play an important role in CO hydrogenation. It seems that both of them are involved in hydrogen dissociation and CO hydrogenation, perhaps via the attack of CO to form formyl, and then being hydrogenated to methoxide, which may be the intermediate of an olefin and paraffin.

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