

Alkylation of Toluene over Basic Catalysts—Key Requirements for Side Chain Alkylation

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In situ infrared spectroscopy was used to study sorption and reaction of toluene and methanol over various basic catalysts (MgO, hydrotalcites, and basic zeolites). The size of the metal cations controls the preference of sorbing methanol or toluene; i.e., the larger the metal cation, the higher the preference for toluene. The key requirements for a good catalyst for side-chain alkylation are (i) sufficient base strength to dehydrogenate methanol to formaldehyde, (ii) stabilization of sorbed toluene and polarization of its methyl group, and (iii) balanced sorption stoichiometry of the two reactants. The formation of the carbon–carbon bond mechanistically resembles an aldol condensation. © 1998 Academic Press

1. INTRODUCTION

Because of its theoretical potential as a novel route to styrene, alkylation of toluene with methanol over basic materials has been studied frequently over the past years (1–6). Despite these efforts, a consensus has not been reached so far concerning the mechanism of the reaction and the role of the catalyst in directing the selectivity toward side chain or ring alkylated products. It is known that basic materials such as Cs⁺- and Rb⁺-exchanged X zeolites catalyze the side chain alkylation of toluene with methanol to styrene, which subsequently can be hydrogenated to ethylbenzene (7–9). Acid materials, i.e., H–Y, H–ZSM5, etc., selectively catalyze ring alkylation to xylenes (10–12). While the rates for ring alkylation are quite high, the rates and yields for side chain alkylation are still unsatisfactory, especially from the point of methanol utilization. A recent study indicated, however, that alkali metal (hydr)oxides supported in zeolite strongly improve the yield of the side chain alkylation products (13). Also, the addition of boron (14) or zinc oxides (15) has a promoting effect on the side chain alkylation.

Two factors have been suggested to be crucial to selective catalysis of side chain alkylation: (i) the presence of active (basic) sites capable of dehydrogenating methanol

to formaldehyde and stabilizing the formaldehyde on the catalyst (8, 16, 17); (ii) spatial constraints as found within zeolite pores and inhibition of toluene rotation in the zeolite cavity (13, 17–19). It has also been suggested that specific steric configurations of acidic and basic sites are crucial for the formation of the required reaction complexes on the zeolite surface (17, 20–27). The base sites activate the carbon atom of the side chain of toluene and the acid sites adsorb and stabilize the toluene (21). Thus, the active center is an assembly of acid and base sites in a cooperative action. In contrast to these quite complex requirements, Giordano (6) suggests that the primary factor governing zeolite activity and selectivity is the overall acid–base strength, expressed as the averaged Sanderson electronegativity of the oxide.

In a previous communication (28), we have reported an *in situ* IR spectroscopic study of the surface chemistry on different alkali-exchanged X zeolites during toluene alkylation. We concluded that in addition to requirements listed above, the balanced sorption stoichiometry of the two reactants and a strong polarization of the methyl group of toluene are indispensable to catalyze side chain alkylation of toluene.

The purpose of the present contribution is to compare the surface chemistry of other basic materials with varying activity (Cs⁺-solid-state-exchanged Y zeolite, MgO, and hydrotalcites with various Al/(Al + Mg) ratios) with that of alkali-exchanged X zeolites and to show that high base strength alone is insufficient for good catalytic properties. It is our goal to outline the requirements of the working catalysts during toluene alkylation. *In situ* IR spectroscopy and kinetic measurements are used to show how chemisorption and stabilization of the reactants at the surface of the different basic materials relate to their catalytic properties.

2. EXPERIMENTAL

2.1. Materials

Ion- (Cs⁺, Rb⁺, K⁺ and Na⁺-) exchanged X zeolites were prepared from Na-X (obtained from Fluka) by conventional cation-exchange procedures using 0.025 M aqueous

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solutions of potassium oxalate, rubidium acetate, or cesium acetate at 353 K. The exchange procedure and the characterization of the samples are described in a previous paper (28). Cesium-solid-state-exchanged zeolite Y was obtained from Prof. Dr. H. G. Karge of the Fritz Haber Institut der Max Planck Gesellschaft (Berlin, Germany). The Si/Al ratio of the zeolite was 2.6 and 100% Cs⁺ exchange was reached. Hydrotalcites with Al/(Al + Mg) ratios of (Ht 0.33) and (Ht 0.2) and MgO with a specific surface area of 200 m²/g were obtained from Prof. A. Corma of the Instituto de Tecnologia Quimica de Valencia (Spain).

2.2. Sorption and Coadsorption Experiments

IR spectra were obtained on a Bruker IFS88 FTIR spectrometer (4 cm⁻¹ spectral resolution). For the sorption experiments, a stainless steel cell with CaF₂ windows that could be evacuated to pressures below 10⁻⁶ mbar was used (for details see Ref. (29)). Before the adsorption was started, the samples were activated *in situ* under vacuum at 773 K for 6 h. The activated sample wafer was then contacted with the appropriate pressure of methanol or toluene (between 10⁻⁴ and 1 mbar) at constant temperature (*T* = 308 K) until adsorption-desorption equilibrium was achieved (monitored by time-resolved IR spectroscopy). For the coadsorption experiments, the catalyst was first equilibrated with one reactant at a partial pressure of 5 × 10⁻³ mbar. Subsequently, the equilibrated material was exposed to 5 × 10⁻³ mbar of the second reactant until adsorption-desorption equilibrium was reached (while keeping the partial pressure of the first reactant constant). Then, the sample was evacuated for one hour at 308 K. The sorbed molecules remaining on the catalyst were removed by temperature-programmed desorption (rate 10 K/min, up to 773 K) while the desorbing species were analyzed by mass spectroscopy.

The gravimetric and calorimetric measurements were performed in a modified SETARAM TG-DSC 111 instrument. The adsorption capacity for toluene and methanol was determined at 5 × 10⁻³ mbar under the same conditions as used for the infrared measurements.

For a typical experiment, approximately 15 mg of the samples was charged into the quartz sample holder of the balance and activated by heating in vacuum (*p* < 10⁻⁶ mbar) with a temperature increment of 10 K/min to 873 K and holding that temperature for 1 h. After cooling to 303 K, toluene was discontinuously dosed into the closed system and equilibrated with the surface. The equilibration was followed by means of heat flow and weight changes. Reversibility was checked through desorption of the alkanes induced by evacuation of the system at several points in one experiment. The experiments were carried out in the pressure range from 10⁻³ to 13 mbar. The pressure was recorded with a BARATRON pressure transducer (type

122A). The adsorption isotherms were determined gravimetrically simultaneously with the differential enthalpies of adsorption. The accuracy of the calorimetric measurements was ±2 kJ/mol.

2.3. Reaction Studies

For the *in situ* reaction studies, an IR cell with the characteristics of a well-stirred continuously operating tank reactor (volume = 1.5 cm³) equipped with $\frac{1}{16}$ " gas inlet and outlet tubings and CaF₂ windows was used (30). To characterize the species sorbed in the material during the catalytic reaction, time-resolved IR spectra were recorded at various reaction temperatures from 373 to 723 K as the activated material was contacted with the reactant stream. The feed gas composition had a partial pressure ratio of toluene/methanol = 45/15 (expressed in mbar) and He was added to 1 bar. The overall flow was 3.5 ml/min. This corresponds to a W/F ratio of 1.8 × 10⁴ g of catalyst · s/mol of toluene + methanol. Simultaneously, samples of the effluent gas stream were collected in sample loops of a multiport valve and subsequently analyzed by gas chromatography (HP5890 II, capillary column DBWAX 30m, FID, He as carrier gas).

Because of the low reactivity of the catalysts, the small weight permissible for an *in situ* infrared experiment, and the minimum flow rates for a good backmixing, only low conversions and yields could be achieved in the IR reactor. Therefore, parallel experiments were performed replacing the IR reactor with a tubular quartz reactor (4 mm inner diameter) in order to be able to directly compare the data to those reported in the literature (7, 9, 13, 31). In these experiments, catalyst powders were loaded into the fixed bed quartz reactor and heated *in situ* at 723 K in flowing He for 2 h before cooling to the reaction temperature (698 K). A liquid mixture of toluene and methanol at a 3:1 molar ratio was then pumped into the reactor system. The reactants were vaporized (partial pressure ratio 45/15 (expressed in mbar)) and then mixed with flowing He to obtain a constant reactor space time. A W/F of 1.2 × 10⁵ g of catalyst · s/mol toluene + methanol was chosen and the reaction was tested at 698 K. The yield was calculated referred to the methanol feed (mol styrene + mol ethylbenzene in the outlet per mol of methanol in the feed) and to the aromatic feed (mol styrene + mol ethylbenzene in the outlet per mol of toluene in the feed). The selectivity was defined as moles of styrene + ethylbenzene formed per mole of toluene reacted (selectivity to side chain alkylation) or moles of xylenes formed per mole of toluene reacted (selectivity to ring alkylation). Other products detected were formaldehyde, dimethyl ether, CO, and H₂O. Note that rates and yields obtained in the latter reactor are in excellent agreement with the values reported in the literature (Table 1), while the selectivities between the two

TABLE 1

Yields Reported in the Literature for the Side Chain Alkylation of Toluene with Methanol on Cs- and Rb-X ($T = 698$ K)

Reference	W/F (g · s/mol)	% Yield (mol styrene + ethylbenzene/ mol methanol)	% Yield (mol styrene + ethylbenzene/ mol of toluene)
Our work	1.2×10^5	7.6	2.5
[7]	1.8×10^5	10	
[9]	6×10^5	10–20	
[14]	1.1×10^5	13	
[13]	1×10^5		0.4–2.75

reactors used in the present study (i.e., the IR reactor and the tubular reactor) were almost identical (Table 2).

3. RESULTS

3.1. Adsorption of the Individual Reactants

The IR spectra of methanol sorbed on different samples are shown in Fig. 1. Table 3 compiles the wavenumbers of the bands of methanol sorbed on the various samples. All the spectra shown in this paper are difference spectra. In this mode of presentation, the bands increasing in intensity after exposing the activated material to the sorbate point upward; the bands decreasing in intensity point downward.

After equilibration at 5×10^{-3} mbar, the stretching vibration of the hydrogen-bonded OH group of methanol appeared as a broad band (between 3500 and 3200 cm^{-1}) with the alkali-exchanged zeolites, and as a combination of several broad bands (between 3600 and 2900 cm^{-1}) with hydrotalcites and MgO. With MgO, additionally, two relatively narrow bands were observed at 3475 and 3618 cm^{-1} . With the nonzeolitic materials a negative peak appeared between 3734–3760 cm^{-1} characteristic of oxide surface hydroxyl

groups in interaction with the sorbate. The C–H stretching vibration bands appeared between 2917 and 2955 cm^{-1} and 2771 and 2839 cm^{-1} (asymmetric and symmetric vibration), the C–H deformation vibration bands between 1451 and 1480 cm^{-1} , and the C–O–H deformation vibration between 1400 and 1420 cm^{-1} . With MgO and hydrotalcite two peaks assigned to C–O stretching vibrations were observed at 1098–1105 and 1045–1065 cm^{-1} . Note that these bands could not be seen with the zeolite samples due to the strong absorption of their Si–O vibrations. All these observed bands for methanol adsorbed on zeolites and metal oxides agree well with results obtained by other research groups (25, 31–33).

The temperature of the desorption maximum of methanol during t.p.d. of methanol decreased in the order MgO, hydrotalcites > Na–X > Rb–X, Cs–X > Cs–Y. With MgO and hydrotalcites the interaction between methanol and the surface was so strong that even at temperatures higher than 773K some methanol-derived compounds remained adsorbed.

The bands of the IR spectra of adsorbed toluene are compiled in Table 4. For toluene sorbed on the zeolitic materials only minor differences in the wavenumbers of the C–C and the ring deformation vibrations (1598, 1494, and 1465 cm^{-1}) were observed. The C–H stretching vibration bands of the aromatic ring (3058–3048 and 3024–3019 cm^{-1}) and the methyl group (2921–2912 and 2874–2857 cm^{-1}) slightly shifted to lower wavenumbers as the size of the cation increased (25). The characteristic bands of the out of plane vibrations were observed between 1700 and 2000 cm^{-1} (34), and were especially well resolved for toluene sorbed on Cs–Y. With the hydrotalcites and MgO the concentrations of toluene sorbed were small compared to the other samples studied. A negative band at 3725–3747 cm^{-1} and a positive band between 3670 and 3700 cm^{-1} were observed in the difference spectra, which varied in parallel in intensity. During t.p.d. of toluene the temperature

TABLE 2

Comparison between the Selectivity (mol %) Obtained in the Side Chain Alkylation of Toluene with Methanol in the IR Reactor ($W/F = 1.8 \times 10^4$ g · s/mol Toluene + Methanol) and in the Tubular Quartz Reactor ($W/F = 1.2 \times 10^5$ g · s/mol Toluene + Methanol, Toluene/Methanol = 3) at 698 K over Different Materials

Sample	Selectivity to side chain alkylation ($W/F = 1.2 \times 10^5$ g · s/mol)	Selectivity to ring alkylation ($W/F = 1.2 \times 10^5$ g · s/mol)	Selectivity to side-chain alkylation ($W/F = 1.8 \times 10^4$ g · s/mol)	Selectivity to ring alkylation ($W/F = 1.8 \times 10^4$ g · s/mol)
Hydrotalcites	traces		traces	
MgO	traces		traces	
Cs–X	78	14	82	10
Rb–X	65	22	70	20
K–X	46	43	41	39
Na–X	3	97	5	95
Cs–Y	—	—	17	83

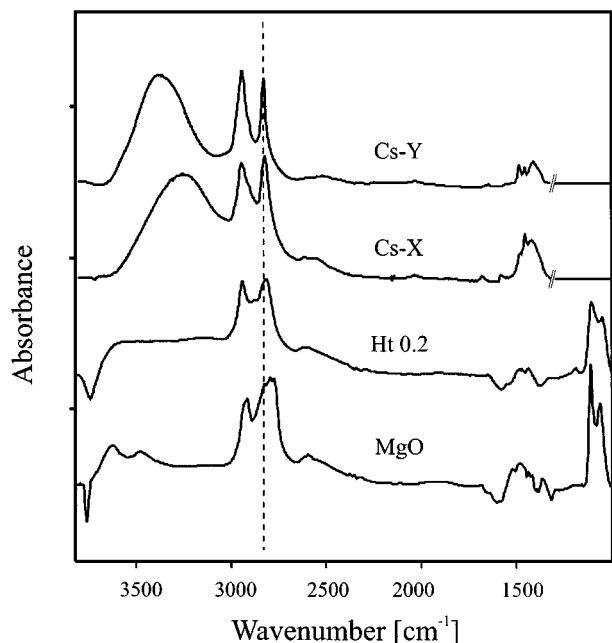


FIG. 1. Difference IR spectra of methanol sorbed on MgO, hydrotalcite, Cs-X, and Cs-Y ($p = 5 \times 10^{-3}$ mbar, $T = 308$ K).

of the desorption rate maximum increased in the order $\text{MgO} < \text{hydrotalcite} < \text{Na-X} < \text{Rb,Cs-X} < \text{Cs-Y}$.

The adsorption isotherms of toluene on Na-X and Cs-X show that the amount of toluene sorbed on Cs-X is larger than on Na-X. The heats of adsorption for Na-X and Cs-X (extrapolated to zero loading) are 76 kJ/mol and 92 kJ/mol respectively, for MgO it is much lower (50 kJ/mol).

3.2. Coadsorption of the Reactants

The IR spectra recorded after coadsorption of the two reactants are compiled in Fig. 2. Only bands characteristic for sorbed toluene and methanol were observed. The bands typical for sorbed toluene (C-H stretching vibrations of the aromatic ring at 3055–3045 and 3025–3020 cm^{-1} , C-H stretching vibrations of the methyl group at 2918–2916

TABLE 3

IR Bands of Methanol Sorbed on Na-X, Cs-X, Cs-Y, Hydrotalcite, and MgO at 5×10^{-3} mbar and 308 K

Sample	$\nu_{\text{O-H}}$ [cm^{-1}]	$\nu_{\text{C-H methyl}}$ [cm^{-1}]
Na-X	3336	2956, 2839
Cs-X	3244	2941, 2820
Cs-Y	3375	2940, 2829
Ht 0.33	3600–2900	2940, 2817
Ht 0.2	3739 (negative band) 3600–2900	2941, 2815
MgO	3740 (negative band) 3600–2900, 3617, 3481 3758 (negative band)	2939, 2917, 2824, 2795, 2772

TABLE 4

IR Bands of Toluene Sorbed on Na-X, Cs-X, Cs-Y, Hydrotalcite, and MgO at 5×10^{-3} mbar and 308 K

Sample	$\nu_{\text{C-H aromatic}}$ [cm^{-1}]	$\nu_{\text{C-H aliphatic}}$ [cm^{-1}]
Na-X	3055, 3024	2921, 2859
Cs-X	3048, 3021	2916, 2857
Cs-Y	3048, 3021	2912, 2874, 2858
Ht 0.2, Ht 0.33	3083, 3053, 3024	2950, 2926, 2871
MgO	3082, 3052, 3025	2958, 2926, 2873

and 2869–2859 cm^{-1} , and C-C ring vibrations at 1495 and 1598 cm^{-1}) were the main spectral features with the Cs^+ exchanged zeolites. On the other hand, the bands characteristic of sorbed methanol (the O-H stretching vibration at 2900–3600 cm^{-1} and the C-H stretching vibrations of the methyl group at 2815–2771 and 2945–2917 cm^{-1}) were the most important ones after coadsorption of methanol and toluene on hydrotalcite and MgO. Indeed, the quantitative evaluation of the IR spectra showed that the ratio of toluene : methanol in the sorbed phase was 1 : 30 with MgO, 1 : 19 with hydrotalcite, 2 : 1 with Cs-X, and 3 : 1 with Cs-Y. T.p.d. of coadsorbed toluene and methanol from the various materials (Fig. 3) also indicated that methanol was the main desorbing species at every temperature with hydrotalcite and MgO, while it was toluene with Cs-X and Cs-Y.

3.3. Reaction Studies

With zeolitic materials reaction products were not detected in the gas phase below 523 K. Above 523 K, the

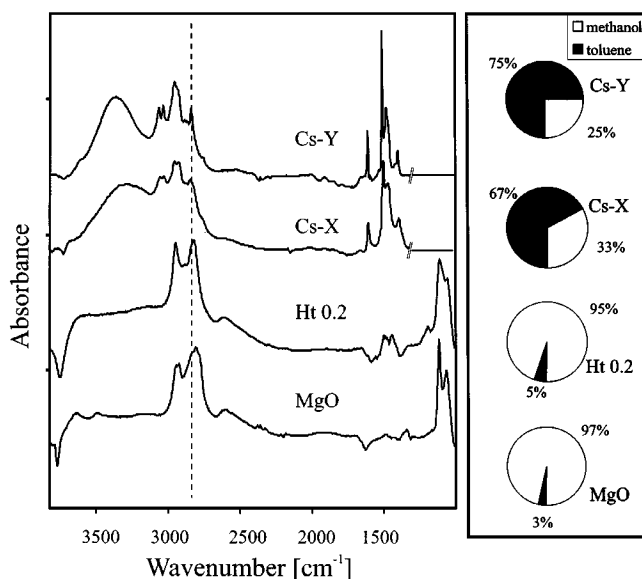


FIG. 2. Difference IR spectra and quantitative evaluation of toluene and methanol occupation after coadsorption of toluene and methanol on MgO, hydrotalcite, Cs-X, and Cs-Y ($p = 5 \times 10^{-3}$ mbar, $T = 308$ K).

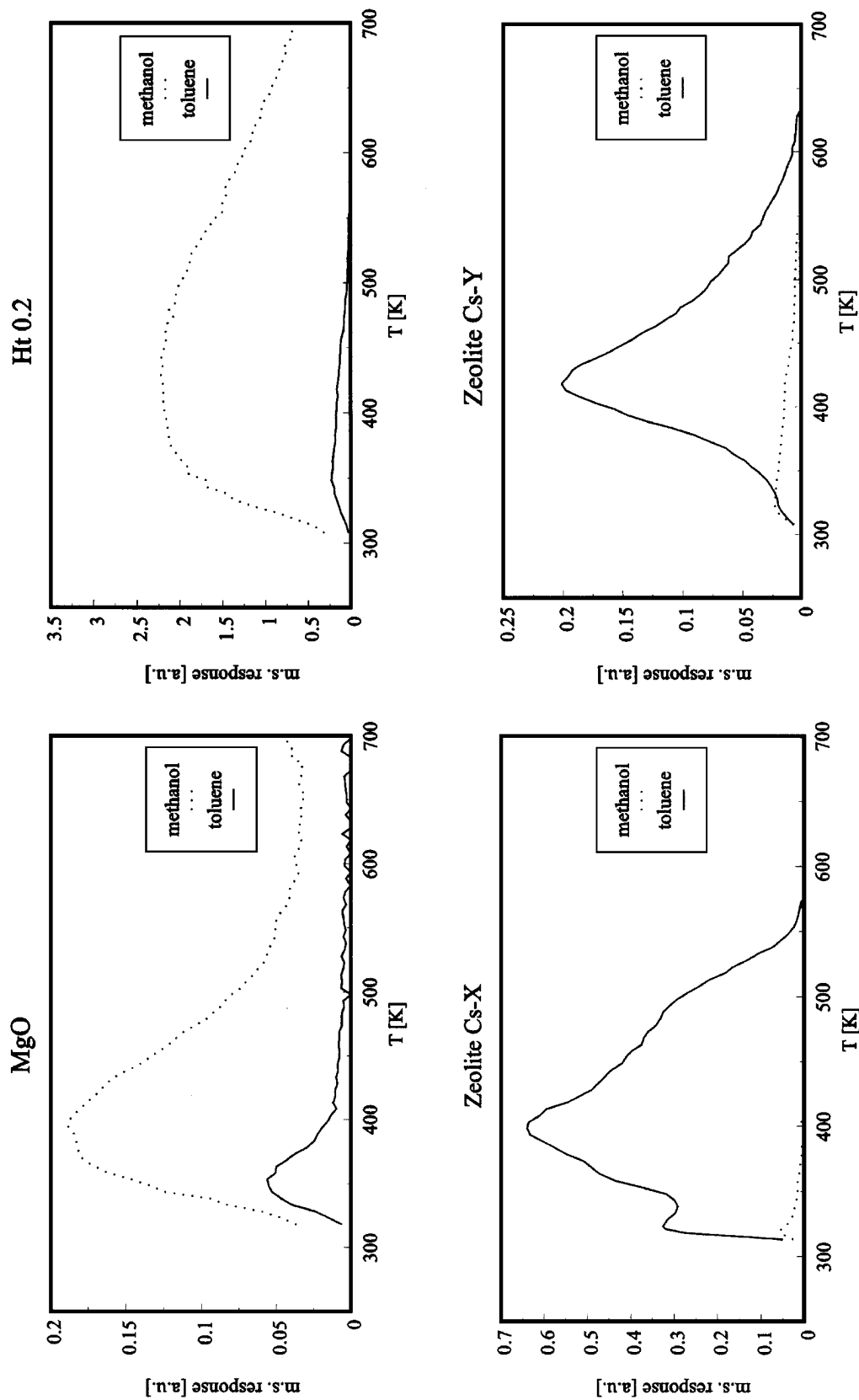


FIG. 3. T.p.d. of toluene and methanol coadsorbed on MgO, hydrotalcite, Cs-X, and Cs-Y.

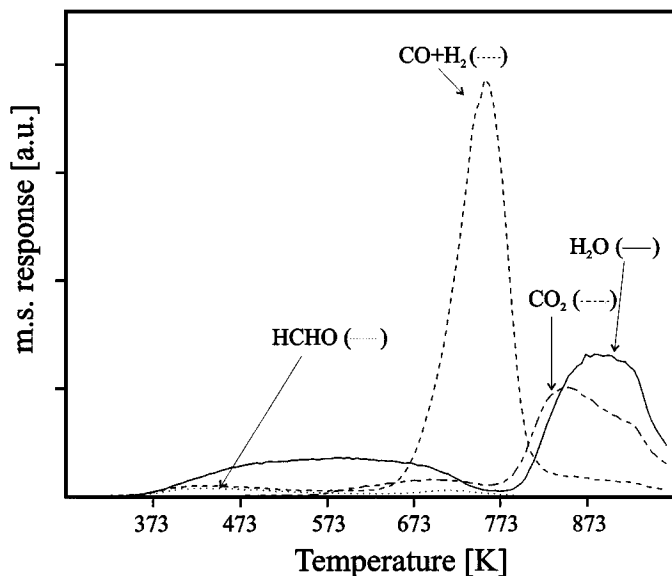


FIG. 4. Products formed during temperature programmed reaction of toluene and methanol over hydrotalcite with an Al/Al + Mg ratio of 0.2. (47 mg of sample, 10 K/min, 6 mbar toluene, 3 mbar methanol).

formation of formaldehyde was observed. Products of the alkylation of toluene with methanol appeared between 573 and 593 K. Depending on the zeolite, side-chain-alkylated (Cs-X) or ring-alkylated products (Cs-Y) were formed (Table 2). The situation was different with the hydrotalcites and MgO. In this case, side-chain-alkylated products were only observed in very low concentrations, the main reaction products being formaldehyde, dimethylether, CO, H₂ and water up to 673 K, H₂ and CO between 673 and 823 K, and CO₂ and H₂O at higher temperatures (see Fig. 4).

The *in situ* IR spectra obtained in the temperature programmed reaction of toluene and methanol over Cs-X and hydrotalcite are shown in Figs. 5 and 6, respectively. With

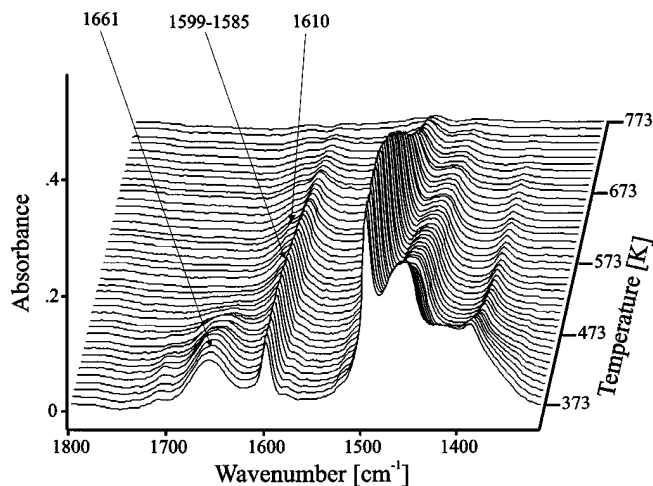


FIG. 5. Difference IR spectra of Cs-X during the reaction of toluene and methanol as a function of the reaction temperature ($T=423-743$ K).

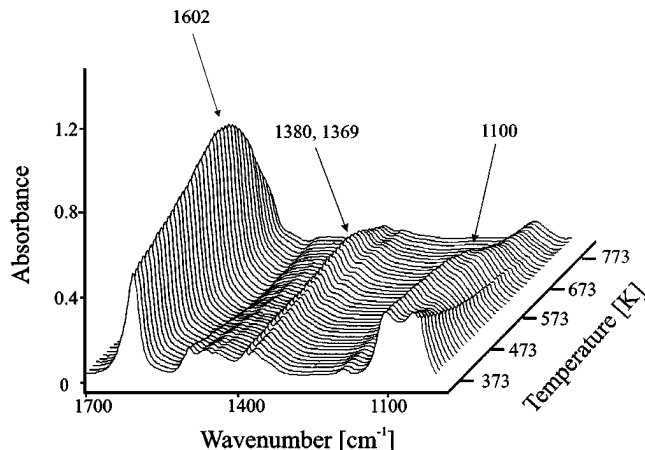


FIG. 6. Difference IR spectra of a hydrotalcite with an Al/Al + Mg = 0.2 during the reaction of toluene and methanol as a function of the reaction temperature ($T=423-743$ K).

Cs-X, at low temperatures, the main bands were characteristic for sorbed toluene, while a new band was observed around 1660–1680 cm⁻¹. This band reached its maximum intensity around 433 K and disappeared completely at 523 K. At higher temperatures another new band (as a shoulder) was observed with Cs-X at 1610 cm⁻¹ (as was previously reported (28) for Na-X). The presence of this band is difficult to unequivocally establish due to the overlap with the band of sorbed toluene at 1600 cm⁻¹. For clarification, Cs-X was exposed only to methanol. It was seen (Fig. 7, line c) that in this case also a band appeared around 1610 cm⁻¹. Note that the shoulder at 1610 cm⁻¹ was observed in the spectra during reaction over Cs-X zeolite but not during reaction over Cs-Y (Fig. 7, line b).

With hydrotalcite (Fig. 6) and MgO, methanol was the main adsorbent and, thus, nearly all bands were related

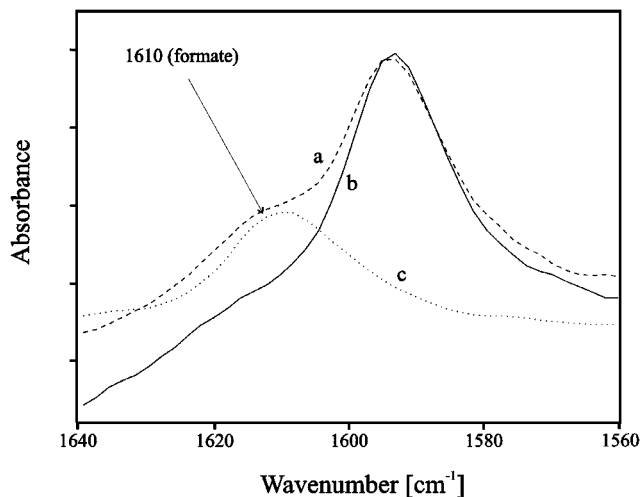


FIG. 7. Difference IR spectra at 643 K of (a) methanol and toluene on Cs-X, (b) methanol and toluene on Cs-Y, (c) methanol on Cs-X.

to methanol and its reaction products. The most intense band appeared at 1602 cm^{-1} , together with two other bands at 1380 and 1369 cm^{-1} (35). These bands (especially that at 1602 cm^{-1}) appeared already at very low temperatures (333 K) and increased in intensity until 673 K . Then, their intensity decreased, but the bands were still visible at 773 K . A new band was also observed at 1089 cm^{-1} and 1118 cm^{-1} (starting from 473 K), reaching its maximum intensity at 673 K , when the bands at 1109 and 1060 cm^{-1} disappeared.

4. DISCUSSION

4.1. Adsorption and Coadsorption of the Reactants

When methanol is sorbed on the alkali-cation-exchanged zeolites (28), all bands typical for hydroxyl and methyl group stretching vibrations shift to lower wavenumbers indicating a weakening of the OH and CH bands due to the interactions with the catalyst. The wavenumbers of the OH stretching vibration band decreased in the order $\text{Cs-Y} > \text{Na-X} > \text{Cs-X}$, Rb-X . This shift results from two effects, i.e., the increasing interaction between the OH groups and the oxygen of the zeolite lattice and the increasing intermolecular interactions between sorbed methanol molecules (36). In the case of methanol sorbed on MgO and hydrotalcites several overlapping broad bands appear indicating strong hydrogen-bonded hydroxyl groups of the surface and of sorbed methanol. The most important suggestion from these results is that the hydrogen bonds of a molecule like methanol become stronger the more polar (in case of the oxygen, the more basic) the surface is.

Note that the wavenumber of the symmetric methyl stretching band decreased in the order $\text{Na-X} > \text{Cs-Y} > \text{Rb-X} > \text{Cs-X} > \text{hydrotalcite} > \text{MgO}$. In line with an earlier paper of Takezawa and Kobayashi (37) this indicates increasing strength of interaction between the lattice oxygens of the catalyst and the hydrogen atoms of the methyl group of methanol. It suggests that MgO ($\nu_{\text{s C-H}} 2795\text{ cm}^{-1}$) is the most basic and Na-X ($\nu_{\text{s C-H}} 2839\text{ cm}^{-1}$) the least basic material.

In the case of the hydrotalcite, the presence of two broad OH stretching vibrational bands reflects well the contribution of the perturbed surface OH groups and the OH group of methanol. An exact contribution is not possible at this point, but previous experience with sorption on acidic zeolites indicates the existence of cyclic sorbed species (38).

For MgO the case is more complex and the relatively narrow bands that appear with the broad bands, show dramatically lower hydrogen-bonding strength and/or dissociation of methanol and the formation of new hydroxyl bands (33, 39). Moreover a significant fraction of the molecules is concluded to be sorbed on Mg^{2+} cations which also should lead to a relatively sharp OH band. The C-H stretching

vibrations at 2939 and 2824 cm^{-1} , appearing as shoulders in Fig. 1, are attributed to a methyl group vibrating rather freely, probably related to the narrow O-H bands observed at higher wavenumber.

The results from the t.p.d. of methanol show that it is bound strongly when the radius of the accessible metal cation is small (MgO, hydrotalcite, and Na-X) and the interaction becomes very weak when the radius is large (Cs-X, Cs-Y). Thus, we conclude that methanol is coordinately bound to the metal cation *via* the lone pair of its oxygen and the strength of the interaction between methanol and the catalyst is mainly determined by this bonding. This is clearly seen when the decreasing strength of methanol sorption with increasing size of the cation in a series of alkali-exchanged X-zeolites is considered (28). The increasing base strength of the lattice oxygen in this series leads to more pronounced hydrogen bonding between the methanol hydroxyl group and the lattice oxygen. However, the contribution of that interaction to the overall strength of sorption is minor. Note that these interactions are most pronounced for the most basic catalysts of this study, i.e., MgO and the hydrotalcites.

The infrared spectra of sorbed toluene show a slightly downward shift of the C-H stretching vibration bands of the aromatic ring and the methyl group as the size of the cation increases. These shifts to lower wavenumbers are attributed to a combination of the strong interactions of the aromatic ring with the cation (acting as electron withdrawing, i.e., electron pair acceptor (40) sites) and to direct interactions with the lattice oxygen. These observations are in line with reports by Barthomeuf *et al.* (41) and Jobic *et al.* (42) on the adsorption of benzene on Na-Y zeolite.

With MgO and the hydrotalcites, only traces of toluene were adsorbed on the hydroxyl groups, giving rise to a band at 3743 cm^{-1} . Upon contact with toluene a band appears at 3670 cm^{-1} (in parallel to the decrease of the band at 3743 cm^{-1}), attributed to the perturbed OH groups hydrogen-bonding toluene. Such hydrogen-bonding interactions with aromatic molecules have been shown to be very weak (43), even when adsorbed on very acidic hydroxyl groups. For the current sample of MgO the low uptake and the dominance of this type of interaction suggests that only few hydroxyl groups and partially unsaturated Mg^{2+} exist on the surface of the sample studied.

In contrast to methanol, the sorption strength of toluene increased with increasing size of the metal cation, as seen from the increasing thermal stability during t.p.d. of toluene when going from MgO, hydrotalcite, and Na-X to Cs-X and Cs-Y. The stronger bonding results from the specific interaction of the aromatic ring with the metal cation. The better the match of the delocalized π -orbitals of toluene (Lewis base) and the orbitals of the electron-pair-accepting alkali cation (Lewis acid), the higher the stability of the bond. Note that this is clearly observed also in more complex

systems, such as the K^+ -channels used by Dougherty *et al.* (44, 45). In consequence, this leads to a low mobility of the aromatic molecules sorbed in alkali-exchanged X zeolites with large cations, as suggested also from earlier NMR studies (19, 46). This low mobility, however, is not the result of the steric constraints in the zeolite pores induced by the larger size of the metal cation, as shown by the similar uptake rates on all samples studied. Note in this context that Bellat *et al.* (47) reported even higher uptake rates for the K-Y/*p*-xylene system than for the Na-Y/*p*-xylene system. The stronger interaction of the larger cations is reflected clearly in the heats of toluene adsorption (76 kJ/mol with Na-X and 92 kJ/mol with Cs-X).

The coadsorption experiments fully confirm the results and discussion. MgO and hydrotalcite preferentially adsorb methanol, while Cs-X and Cs-Y adsorb mainly toluene. For the hydrotalcites and MgO, 95–97% of sorption capacity is taken up by methanol, while with Cs-Y 75% of the sorbed molecules are toluene.

4.2. Reaction Studies

Previous reaction studies demonstrated that depending on the alkali ion exchanged into the X-zeolite, side chain or ring alkylation is preferred. X zeolites with larger cations (preferentially adsorbing toluene over methanol) show high selectivity to styrene and ethylbenzene. The more acidic X zeolites (i.e., those with smaller metal cations and preferentially sorbing methanol over toluene) show high selectivity to xylenes (see, e.g., Palomares *et al.* (28)).

Hydrotalcites and MgO readily catalyze methanol dehydrogenation; i.e., formaldehyde and its decomposition products were observed in adsorbed state and in the gas phase. After contact with the reactant mixture chemisorbed formaldehyde (formate bands at 1610–1602 cm^{-1} (39)) was the most abundant surface species. The formation of CO and H_2 was observed as the formate decomposed (673 K). Other CO containing compounds adsorbed at different positions (as evidenced by bands at 1109 and 1060 cm^{-1}) were also seen. With increasing temperature these compounds transform to surface species characterized by bands at 1089 and 1118 cm^{-1} (mixture of carbonate, methoxy, etc.) (33) and finally decompose into CO_2 and H_2O at high temperatures (773 K). In the temperature interval monitored the surface concentration of toluene was minimal. Thus, we conclude that the low toluene concentration prevents an appreciable production of ethylbenzene.

In contrast, with Cs-Y strong sorption of toluene side was observed (see Figs. 2 and 3). However, while formate-type species are present after sorption of methanol on Cs-X (see, e.g., Ref. (32)), they were not observed with Cs-Y (see Fig. 7). This implies that Cs-Y was unable to dehydrogenate/activate methanol. Thus, we attribute the absence of catalytic activity for side chain alkylation to the absence of chemisorbed formaldehyde. This contrasts with

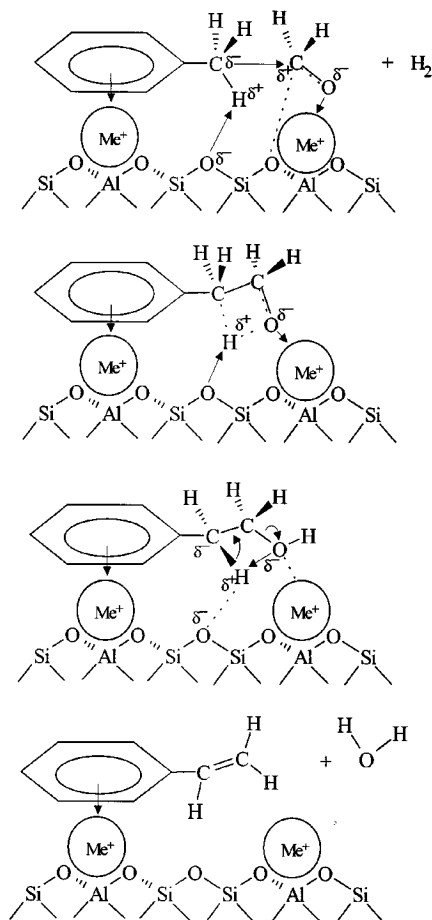
earlier reports of Yashima *et al.* (48) and Wieland *et al.* (49), who reported formaldehyde formation and subsequent side chain alkylation of toluene. We attribute this different behavior to the existence of CsO moieties in the zeolites used by the above-mentioned authors (48, 49), in accordance with Hathaway *et al.* (50). The absence of such very basic oxide clusters leaves the parent Cs-Y zeolite inactive for methanol dehydrogenation. Note in this context that Lavalley *et al.* (31) did not mention any formaldehyde formation on Cs-Y at elevated temperatures (623 K).

It should be emphasized that with Cs-X zeolites a significant fraction of the sites were interacting with toluene (see Figs. 2 and 3) and sorbed formate species were observed. Both materials showed an appreciable activity for side-chain alkylation. Thus, we conclude that from the basic materials reported in this work, only Cs-X possess the adequate balance of both catalytic functions to catalyze the side-chain alkylation of methanol. MgO, hydrotalcites, and Cs-Y were either unable to bind toluene sufficiently or did not transfer methanol into its dehydrogenated state.

5. CONCLUSIONS

The present study, demonstrates that several requirements have to be met to successfully catalyze the side chain alkylation of methanol. The catalyst needs to (i) have sufficient base strength to dehydrogenate methanol to formaldehyde, (ii) stabilize toluene on the surface or in the pores and activate its methyl group, and (iii) establish adequate sorption stoichiometry between toluene and methanol. Only materials which provide all these characteristics show appreciable catalytic activity.

These requirements lead us to suggest a pathway for the reaction (Scheme 1) similar to an aldol-type condensation, which was discussed in detail in Ref. (28), as also postulated by Itoh *et al.* (21). One elementary step is the abstraction of the hydrogen from methanol adsorbed on the basic materials leading to the formation of formaldehyde and formates with a C-atom positively polarized. Note that this does not require redox properties in the oxide catalysts (see, e.g., Ref. (51)). In a parallel reaction step, toluene is strongly retained on the large cations due to the interactions of the toluene π -electrons (electron pair donor) and the cation (electron pair acceptor). This interaction withdraws electron from the aromatic ring and facilitates the polarization of the methyl C-H, much as an electron withdrawing substituent (e.g., a nitro group) on the aromatic ring would (40, 51). Additionally the methyl group of toluene interacts with the oxygen atoms of the basic framework further polarizing the methyl C-H bond. Note that this leads in the transition state (when the hydrogen is being split off as H^+) to a negatively charged methyl carbon. Under these conditions, the positively charged C atom of formaldehyde would react with the activated carbon atom of toluene to



SCHEME 1

form the new carbon-carbon bond at the methyl group. Most likely the reaction would proceed *via* a concerted mechanism avoiding the existence of long lived ionic intermediates. We would emphasize the strong analogy to a classical aldol condensation by stressing the improved ease of that reaction if an electron withdrawing group is placed on the aromatic ring (51).

The elementary step mentioned first may proceed on alkali-cation-exchanged X zeolites, hydrotalcite, and MgO, but not with Cs-Y (as it has an insufficient base strength); the other is only possible with basic materials having large accessible cations, such as the Cs⁺ cations in the exchanged X and Y zeolites, but not with hydrotalcite and the MgO studied in the present report. This is not so much related to the base strength of the lattice oxygen, but to the inability to retain and polarize toluene under reaction conditions. Note that Cs-X is the only material reported here that fulfills both conditions. These results also demonstrate that side chain alkylation does not depend solely on basic properties of a catalytic material and is, hence, inadequate for probing the base strength of unknown materials.

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