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Comments on the use of 2-methylbut-3-yn-2-ol decomposition as a probe reaction for the potential reactivity Mg–Al hydrotalcites as base catalysts

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Mg:Al hydrotalcites (Mg:Al ratios 3:1, 3:2 and 4:1) have been characterised using the decomposition of 2-methylbut-3-yn-2-ol as a probe reaction for the acidic/basic properties. The hydrotalcites were used either as synthesised, or following calcination at 225 and 450 °C. All gave almost exclusively of base-catalysed products (98–99%) and a very small amount of acid-catalysed products (1–2%). For this probe reaction only slight differences in reactivity to the probe molecule were observed. The materials were also investigated for the Meerwein–Ponndorf–Verley reduction of benzaldehyde using a range of primary and secondary alcohols. In contrast to the relative reactivity for the probe reaction, significant differences in both activity and selectivity were observed for the reduction of benzaldehyde. The materials calcined at 450 °C were ca. 3 times more active on the basis of the initial rate of reaction compared with the non-calcined materials. Secondary alcohols were the most reactive and gave benzyl alcohol as the exclusive product, whereas primary alcohols also gave by-products due to ester formation and aldol condensation reactions and the structure of alcohol controlled the product selectivity in a manner consistent with the hydrogen donating properties of these alcohols. Consequently although the use of probe reactions can be instructive in determining the relative concentrations of acid and base sites, unfortunately relative reactivity profiles cannot be used predictively and this is discussed in terms of the adsorption of the probe reactant.

KEY WORDS: magnesium aluminium hydrotalcites; 2-Methylbut-3-yn-2-ol decomposition; Meervein–Ponndorf–Verley reduction; benzaldehyde reduction.

1. Introduction

In recent years, there has been considerable interest shown in the design of suitable heterogeneous acidic, basic and acid/base catalysts [1] for the replacement of homogeneous catalysts that are currently used in industry [2]. This has led to a marked increase in the study of heterogeneously base-catalysed reactions [3–10] since these are less well developed compared with heterogeneously acid catalysed processes [1,2]. In this respect, there has been growing interest in the use of hydrotalcites as catalysts, since they are known to comprise both acidic and basic sites [11,12]. Consequently, there has been a requirement to readily characterise the relative concentration of acidic and basic sites in these and related bifunctional materials. In this respect, the decomposition of model reactants such as 2-methylbut-3-yn-2-ol (MBOH) has been used [13–15], since different products arise from the reaction at acidic, basic or amphoteric sites. Previously, we have studied the decomposition of MBOH as a probe reaction for acidic and basic catalysts for condensation reactions, e.g. the self condensation of acetone [16]. We concluded that, for this type of reaction, the usefulness of MBOH as a probe reactant was limited, since the reaction data gave a linear Constable-Cremer plot [17] which has been interpreted as being caused by the enthalpy of adsorption of MBOH dominating the energetics of the decomposition reactions. A similar problem arises with the study of condensation reactions since the products have higher adsorption enthalpies than the reactants. In view of these earlier observations, we have now studied the usefulness of the MBOH decomposition reaction as a model reaction to characterise a range of hydrotalcites. Since we have shown that the enthalpy of adsorption is an important factor controlling the kinetics observed for MBOH decomposition, the hydrotalcites were studied as catalysts for a reaction in which the reactants and products have similar enthalpies of adsorption and, consequently, the adsorption enthalpies should not be expected to dominate the observed reaction rates. We have selected the Meerwein–Ponndorf–Verley (MPV) reduction of benzaldehyde using alcohols, since this reaction involves a simple hydrogen transfer MPV reduction has been well studied previously [11,12,18–33] [34,35] and is a useful

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model reaction concerning hydrogen transfer. In this paper, we present and contrast the results for the comparative study for the reaction of MBOH and benzaldehyde/alcohol mixtures.

2. Experimental

2.1. Mg-Al hydrotalcite preparation

Hydrotalcites with Mg:Al atomic ratios of 3:1, 3:2 and 4:1 were prepared using a standard aqueous co-precipitation method at constant pH, temperature. An aqueous solution of the metal nitrates in a desired molar ratio (Mg/Al = 3/1; 3/2 and 4/1) with a total concentration of 1.5 M was mixed slowly with continuous stirring with an alkaline solution of Na_2CO_3/NaOH, (carbonate concentration: mol ratio CO_3^{2-}/Al^{3+} = 2). The pH of the mixture was kept constant, typically at values between 9 and 10, by adjusting the flow rate of the alkaline solution. The temperature was maintained at 37 °C. Following this addition, which resulted in the formation of a heavy slurry, the mixture was aged at 65 °C for 18 h with stirring, to facilitate the selective growth of the precipitated hydrotalcite phase. The slurry was then cooled to 25 °C, filtered, and washed with water and dried at 90 °C for 12 h.

2.2. Characterisation methods

Powder X-ray diffraction was performed using an ENRAF Nonius FR 590 X-ray powder diffractometer, using a Cu-Kα source fitted with an Inel CPS 120 hemispherical detector. BET surface area measurements using nitrogen adsorption were carried out using a Micromeritics Gemini 2365 instrument. Scanning electron microscopy (SEM) measurements were carried out using a Cambridge Instruments Stereoscan 360 scanning electron microscope. Thermal gravimetric analysis (TGA) analysis was performed using a Perkin Elmer Thermogravimetric Analyzer TGA 7 instrument in a nitrogen atmosphere.

2.3. Catalyst testing

2.3.1. Reaction of 2-methylbut-3-yn-2-ol (MBOH)

MBOH (Aldrich) was fed using a calibrated syringe pump at a rate of 2.5 g h^{-1} to a vaporiser and mixed with helium (15 mL min^{-1}). The reactants were fed *via* heated lines to a laboratory microreactor containing heated catalyst (1.0 g) diluted with glass beads (Sigma, 710–1180 μm). The products were collected following cooling of the exit gases and analysed using gas chromatography and the carbon mass balance was typically 97 ± 5% depending on the level of coke deposition.

2.3.2. Meerwein–Ponndorf–Verley reduction of benzaldehyde

Benzaldehyde (0.006 mol, Aldrich) was refluxed with an alcohol (0.12 mL) and catalyst (0.5 g) in a round-bottomed flask. Samples were withdrawn at specified times and were analysed using gas chromatography.

3. Results and discussion

3.1. Hydrotalcite synthesis and characterisation

Hydrotalcites have a general formula $[M^{z+}_{1-x}M^{3+}_x(OH)_2]^{b+}$ $[A^{n-}_{b/n}]mH_2O$, where M = metal, A = interstitial anions, and b = x or $2x - 1$ and z = 2 or 1, and are known to exhibit basic properties, but tend to be poorer base catalysts compared with the mixed oxides that can be obtained from their calcination [11,12]. It is considered that the presence of interstitial water molecules effectively blocks the access of reactants to the active sites, thereby resulting in poorer activity and calcination of the samples as a means of controlled activation can give enhanced reactivity. To investigate the effect of calcination, Al/Mg hydrotalcite materials were synthesised with cation ratios of Mg_3Al, Mg_3Al_2 and Mg_4Al and the materials were calcined for 24 h at 225 and 450 °C so that, including the non-calcined samples, a set of nine materials was prepared in all. The set of nine hydrotalcites was characterised using powder X-ray diffraction. Representative diffraction patterns for the Mg_3Al_1 sample are shown in figure 1, since the patterns are very similar for the three sets. The three dried samples all give the powder X-ray diffraction patterns that are characteristic of the hydrotalcite. Calcination at 225 °C causes partial collapse of the structure and the reflections are broadened indicating the formation of a less crystalline material with the possible introduction of defects. Calcination at 450 °C causes further collapse of the structure and all the materials give a set of broad bands with different

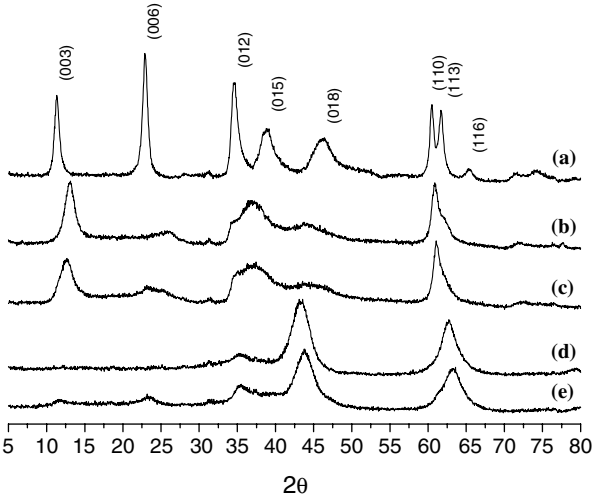


Figure 1. Powder X-ray diffraction patterns for Mg_3/Al_1 hydrotalcites (a) initial; (b) calcined at 225 °C for 20 h; (c) calcined at 225 °C then refluxed in EtOH for 24 h; (d) calcined at 450 °C for 20 h; (e) calcined at 450 °C then refluxed in EtOH for 24 h.

intensities. It is therefore apparent, as expected, that calcination at 225 and 450 °C has a marked effect on the structure of the hydrotalcites.

Calcination at 225 and 450 °C leads to an increase in the total surface area (table 1). As the hydrotalcites were to be used as catalysts for the reactions of alcohols it can be expected that the interaction with the alcohol might be expected to affect the structure. To model this the hydrotalcites were refluxed with ethanol for 24 h. Only minor changes in the X-ray diffraction pattern were observed (figure 1), namely the observation of a broad diffraction line at $2\theta = 14.1°$ in some samples. It is, therefore, concluded that the hydrotalcite samples are reasonably stable under these reaction conditions. In addition. the set of hydrotalcite samples before and after refluxing in ethanol for 24 h were analysed using TGA (figure 2). Calcination of the hydrotalcite at 225 and 450 °C leads to a marked decrease in the weight loss observed during TGA as is expected from the loss of water from the material. Refluxing in ethanol partially restores the weight loss for both calcination temperatures. These data indicate that during the reaction with alcohols, some structural changes with respect to the surface hydroxyl groups and adsorption of reactants can be expected. Consequently, comparison of catalytic activity for reactions of hydrotalcites with alcohols is best made on the basis of initial rates since these can be considered to be more representative of the state of the catalyst following calcination

Table 1
Surface area data for hydrotalcites

Treatment	Hydrotalcite Surface Area/m^2 g^{-1}		
	Mg_3Al_1	Mg_3Al_2	Mg_4Al_1
Non-calcined	54	72	37
Calcined 225 °C	70	92	40
Calcined 225 °C + Reflux[a]	56	83	37
Calcined 450 °C	103	152	55
Calcined 450 °C + Reflux[a]	54	113	84

[a] sample refluxed in ethanol for 24 h.

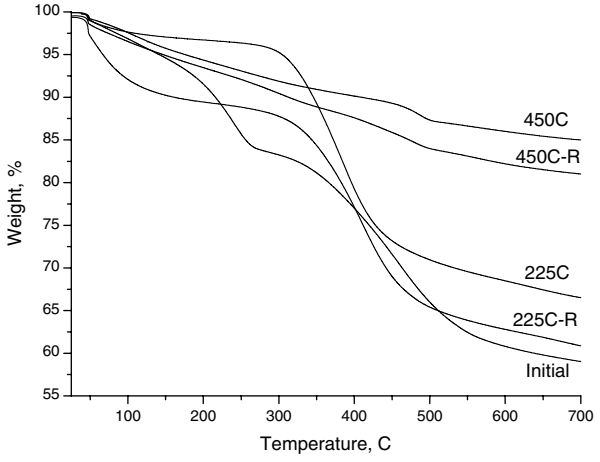


Figure 2. TGA data for hydrotalcite materials Mg_3Al_1, R denotes refluxed in ethanol for 24 h.

3.2. Reaction of 2-methylbut-3-yn-2-ol

The set of nine hydrotalcites was then characterised using the decomposition of MBOH, to characterise the acid and base sites on the catalyst surfaces. Representative data are shown in figure 3 for the Mg_3Al_1 hydrotalcite, since all three sets of samples give similar results. It is apparent that all the hydrotalcite samples behave very similarly to the reaction of this probe molecule at 180 °C, and there are only subtle differences between the samples. The non-calcined hydrotalcites show the highest initial activity, with MBOH conversion of ca. 90% but, within experimental error, there is no difference between the samples. The calcined materials tend to show a lower initial MBOH conversion, typically

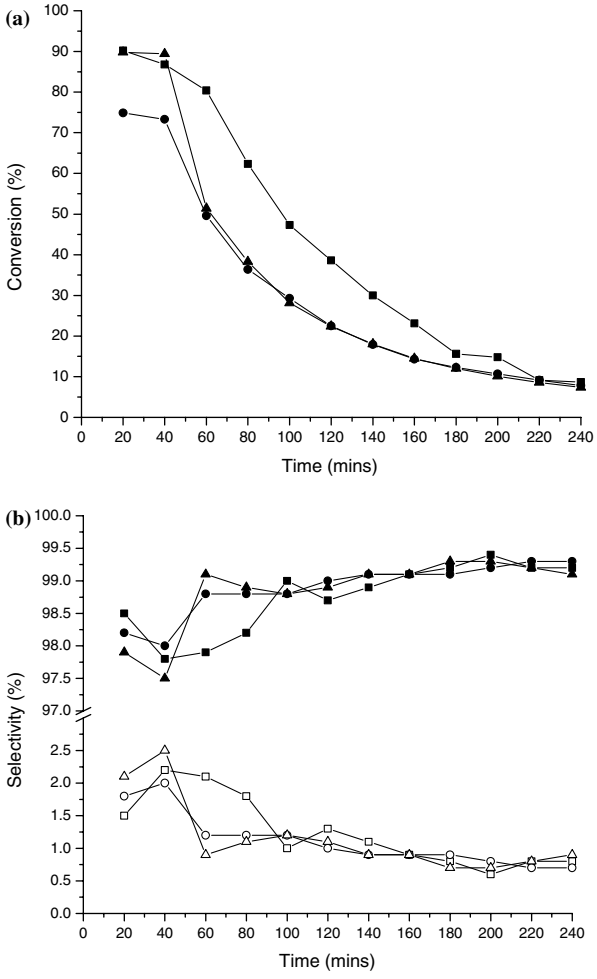


Figure 3. Conversion of MBOH over Mg_3Al_1 hydrotalcite catalysts at 180 °C. (a) conversion: ■ non-calcined; ▲ calcined 225 °C; ● calcined 450 °C; (b) selectivity : closed symbols = selectivity to base-catalysed products; open symbols = selectivity to acid-catalysed products.

ca. 80% under these reaction conditions. For all samples, a rapid deactivation in the MBOH conversion was observed, but this had no effect on the product selectivity. All the samples were predominantly basic (figure 3), giving ≥98% selectivity to the products of base catalysed decomposition of MBOH (i.e. acetone), and ca. 2% selectivity to the products of the acid catalysed reaction (i.e. 3-methyl-3-buten-1-yne and 3-methyl-2-butenal). Analysis of the hydrotalcites using powder X-ray diffraction following the reaction confirmed that the catalyst structure was unchanged. However, the catalysts all contained carbon (ca. 1–2 wt%) as has been noted in our previous studies [16] Since the catalyst selectivity did not change markedly during the deactivation (figure 3), it is concluded that the deactivation is due to the deposition of carbonaceous material on the surface of the catalyst. This is probably due to either acid or base catalysed polymerisation of MBOH or the reaction products. Based on the probe reaction with MBOH, it is concluded that the hydrotalcite materials were predominantly basic with a low concentration of acid sites present on the surface; however, it is clear that the MBOH reaction could not distinguish between the reactivity of these materials and, in particular, the differences associated with calcination of the samples.

3.3. *Meerwein–Ponndorf–Verley reduction of benzaldehyde*

The set of nine hydrotalcites were investigated for the MPV reduction of benzaldehyde with a range of primary and secondary alcohols, and the results are summarised in tables 2 and 3. Interestingly, the non-calcined hydrotalcites and the samples calcined at 225 °C gave identical catalytic performance for this reaction, within experimental error and, hence, only the data for the sample calcined at 225 °C are presented. It is apparent that the most active hydrotalcite catalysts for the reduction reaction are the materials that have been calcined at 450 °C. The catalysts were examined after reaction using powder X-ray diffraction and no significant changes in the patterns of the hydrotalcites were observed compared with the X-ray diffraction pattern of the sample before reaction.

The rates of reaction are in line with the hydrogen donating properties of the alcohols. In particular, the secondary alcohols are much more reactive than primary alcohols (Table 3) which is consistent with the recent observations of Corma *et al.* [30]. However, the conversion data with time-on-line do not fit simple pseudo-first-order kinetics as could be expected for the reaction with the alcohol in 20-fold molar excess. This indicates that it is possible that preferential adsorption of the reactants or products onto the catalyst surface may be occurring. These effects have been noted previously for zeolite catalysts, when used for condensation reactions with liquid reactants, by Derouane *et al.* [32,33].

It is interesting to note that the selectivity observed, within experimental error, for the reaction of the hydrotalcites (non-calcined or calcined at 225 °C) is controlled only by the nature of the alcohol. Representative data are given in figure 4. It is striking to note that the secondary alcohols give 100% selectivity to benzyl alcohol as has been observed for other hydrotalcites by Corma *et al.* [30] In addition, the selectivity was not observed to vary with the reaction time or conversion and the data shown in figure 4 are characteristic of all the reaction times. The selectivity for benzyl alcohol observed with the primary alcohols are all very similar, ca. 70–80% and the formation of the by-products of the aldol condensation or ester formation (Scheme 1) occur at similar rates for most of the alcohols. As the carbon number increases for the primary alcohols, for C_{4+}, the reactivity decreases. Comparison of propanol, prop-2-en-1-ol and 2-methylpropan-1-ol shows that both the reactivity and selectivity to benzyl alcohol decrease in the order:

$$2-\text{methylpropan-1-ol} > \text{prop-2-en-1-ol} > \text{propanol}$$

Again, this is consistent with the hydrogen donating properties of these alcohols.

The selectivities observed with the hydrotalcite samples calcined at 450 °C are markedly different than those of the other samples (figure 5) except, as expected, 100% selectivity to benzyl alcohol was still observed with the secondary alcohols. For the primary alcohols, the selectivity to the by-products is enhanced with the hydrotalcites calcined at 450 °C; in particular for the products of aldol condensation (Scheme 1). As noted earlier, the reaction of MBOH did not show any marked differences in the selectivities for acid/base products for the hydrotalcites calcined at different temperatures.

The observation that calcination of MgAl hydrotalcites at 450 °C significantly increases the reactivity for the Meervwein–Ponndorf–Verley reduction of alcohol is consistent with the previous finding of Figueras and co-workers [11, 12]. They concluded that the enhanced reactivity is due to a synergy between Brønsted and Lewis acid sites.

It is clear that using the reaction of MBOH it is not possible to discriminate between the reactivity of calcined and non-calcined hydrotalcites, whereas for the MPV reduction of benzaldehyde very clear differences in reactivity are observed. As noted earlier, since the hydrotalcites are readily deactivated during the reaction with MBOH, it is more instructive to compare the relative reactivities on the basis of the initial rates for the conversion of MBOH over the hydrotalcite catalyst with the initial rates for the MPV reaction and these data are given in table 4. Clearly, MBOH is much more reactive when tested as a gas phase reactant, when compared with the reaction of benzaldehyde with alcohols in the liquid phase, even when the reaction temperature is taken into account (e.g. compare the reactivity of

Table 2
Reaction of benzaldehyde with primary alcohols using hydrotalcite catalysts

Alcohol	Reaction temperature/°C	Reaction time/h	hydrotalcite[b]					
			Mg_3Al_1		Mg_3Al_2		Mg_4Al_1	
			225 °C	450 °C	225 °C	450 °C	225 °C	450 °C
ethanol	78.5	1	4	8	4	8	4	10
		5	18	30	17	28	19	32
		10	31	56	30	50	32	58
propanol	97	1	3	11	3	10	4	13
		5	17	24	17	23	19	27
		10	32	40	29	41	34	44
prop-2-en-1-ol	97	1	5	10	5	9	5	12
		5	19	42	18	41	20	44
		10	45	68	40	66	48	72
butan-1-ol	117	1	4	15	4	12	5	18
		5	13	39	12	35	15	45
		10	34	72	32	69	38	81
2-methylpropan-1-ol	108	1	5	15	5	12	7	17
		5	13	65	10	63	15	34
		10	35	83	31	81	41	85
pentan-1-ol	137	1	4	14	4	14	4	16
		5	10	49	8	43	12	50
		10	28	77	26	70	30	79
hexan-1-ol	158	1	3	13	3	12	4	15
		5	12	42	12	41	13	44
		10	22	68	20	66	27	72
octanol	194	1	2	9	2	8	4	10
		5	15	40	14	41	16	43
		10	24	49	23	58	28	65

[a] Benzaldehyde (0.006 mol), alcohol (0.12 mol) and catalyst (0.5 mol) refluxed. Data presented as benzaldehyde conversion.
[b] Non-calcined and 225 °C calcined hydrotalcites gave the same conversion within experimental error.

Table 3
Reaction of benzaldehyde with secondary alcohols using hydrotalcite catalysts

Alcohol	Reaction temperature/°C	Reaction time/h	hydrotalcite[b]					
			Mg_3Al_1		Mg_3Al_2		Mg_4Al_1	
			225 °C	450 °C	225 °C	450 °C	225 °C	450 °C
propan-2-ol	82.4	1	5	24	4	10	6	26
		5	34	62	32	41	36	66
		10	65	100	61	72	68	100
butan-2-ol	99.5	1	4	32	5	25	5	33
		5	24	100	21	76	26	100
		10	56	100	49	100	59	100

[a] Benzaldehyde (0.006 mol), alcohol (0.12 mol) and catalyst (0.5 mol) refluxed. Data presented as benzaldehyde conversion.
[b] Non-calcined and 225 °C calcined hydrotalcites gave the same conversion within experimental error.

MBOH at 180 °C with the reactivity of octan-1-ol at 184 °C). The initial rate for the MPV reaction decreases with increasing carbon chain length of the alcohol. However, it is apparent that, for MBOH decomposition, the highest initial rate is observed with the non-calcined hydrotalcite whereas, for the MPV reduction of benzaldehyde, the highest initial rate is observed with the hydrotalcites calcined at 450 °C. In addition, the MBOH reaction does not discriminate between the hydrotalcite samples markedly, whereas there are marked differences in reactivity for the reduction of benzaldehyde. Indeed, the difference in activity for the MPV reaction varies by a factor of ca. 3. This demonstrates a significant limitation for the use of probe reactions, such as MBOH, as a means of evaluating the reactivity of materials as potential base or acid catalysts. Although probe reactions are an important characterisation tool it is clear that they can only be used in a

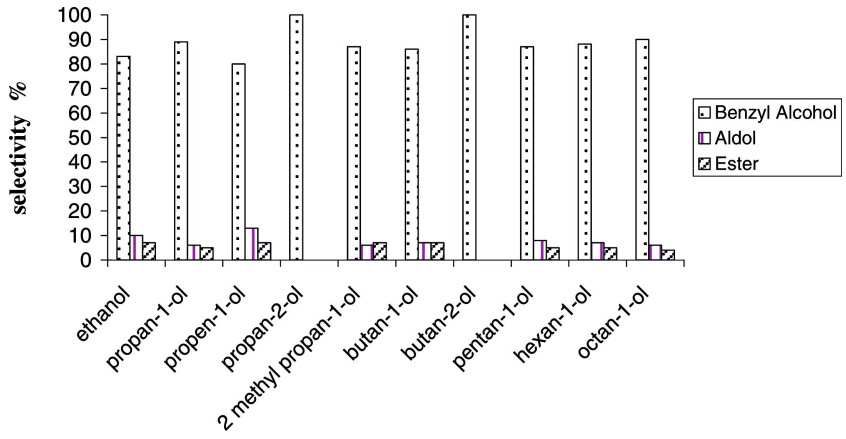
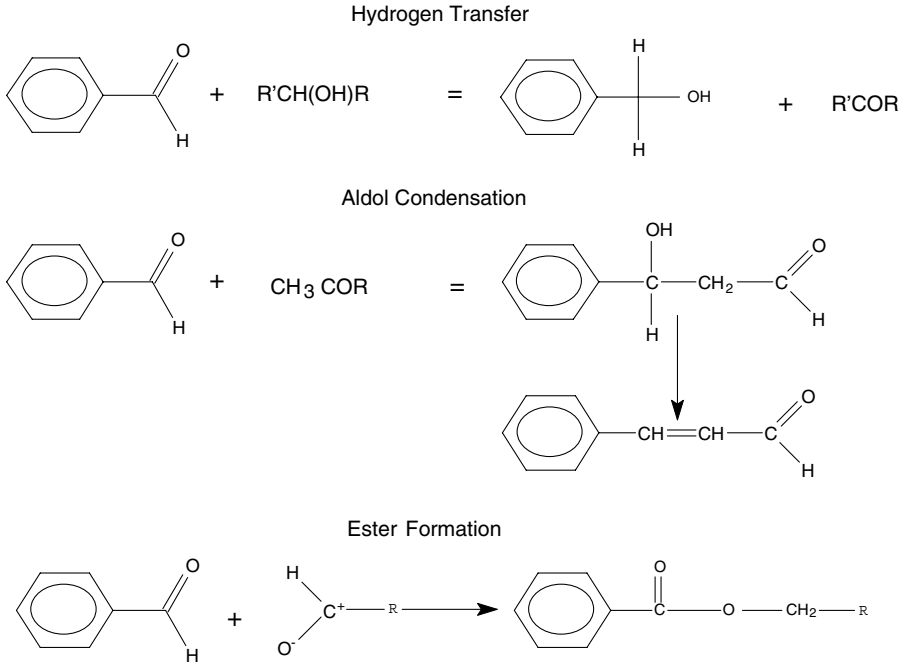


Figure 4. Selectivity of products for reaction of benzaldehyde with alcohols hydrotalcites (non-calcined and calcined 225 °C).



Scheme 1.

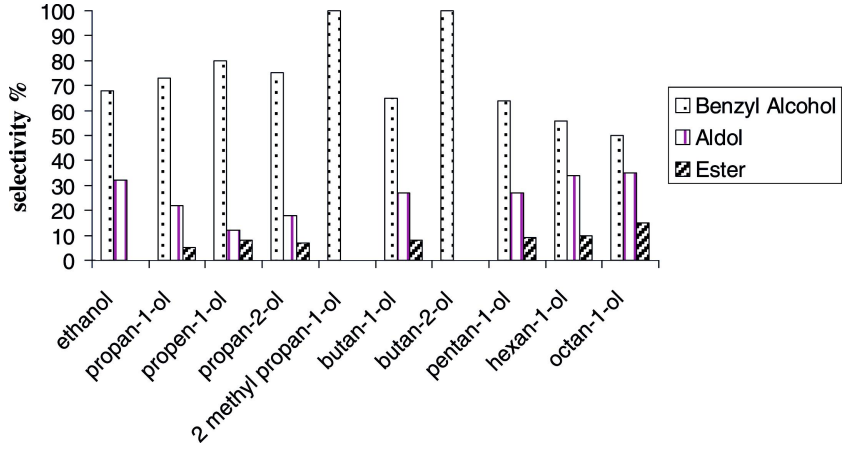


Figure 5. Selectivity of products for reaction of benzaldehyde with alcohols over Mg_3Al_1 hydrotalcite calcined at 450 °C.

Table 4
Initial rates for alcohol conversion

Hydrotalcite	Initial rate/10^{-7} mol/g catalyst/s				
	MBOH[a] 180 °C	butan-1-ol[b] 117 °C	butan-2-ol[b] 99 °C	hexan-1-ol[b] 158 °C	octan-1-ol[b] 194 °C
Mg_3Al_1	750	1.3	1.3	1.0	0.6
Mg_3Al_1 (225 °C)	750	1.3	1.3	1.0	0.6
Mg_3Al (450 °C)	620	4.8	10.2	4.2	2.9
Mg_3Al_2	730	1.3	1.3	0.6	1.0
Mg_3Al_2 (225 °C)	600	1.3	1.6	1.0	0.6
Mg_3Al_2 (450 °C)	600	3.8	8.0	3.8	2.9
Mg_4Al_1	750	1.3	1.9	1.3	1.3
Mg_4Al_1 (225 °C)	660	1.6	1.6	1.3	1.3
Mg_4Al_1 (450 °C)	650	5.8	10.6	4.8	3.2

[a] MBOH conversion at 180 °C, initial rate at 20 min time-on-line.
[b] Reaction of benzaldehyde with alcohols initial rate at 1 h reaction time.

specific manner to determine the relative concentrations of acidic and basic sites. As we have noted previously [16] the heat of adsorption of MBOH can dominate the reactivity of this probe molecule and this then masks any potential differences in the reactivity that could be expected for the different oxides as catalysts for the decomposition reaction, and consequently their use for catalyst evaluation must be used with some caution.

Acknowledgments

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References

[1] K. Tanabe and W.F. Hölderich, Appl. Catal. A 181 (1999) 399.
[2] F. King and G.J. Kelly, *Catal. Today* (2002) 75..
[3] S.C. Luo and J.L. Falconer, J. Catal. 185 (1999) 393.
[4] J.J. Spivey, M.R. Gogate, J.R. Zoeller and R.D. Bolberg, Ind. Eng. Chem. Res. 36 (1997) 4600.
[5] A.G. Panov and J.J. Fripiat, Catal. Lett. 57 (1999) 25.
[6] A. Philippou and M.W. Anderson, J. Catal. 189 (2000) 395.
[7] A. Guida, M.H. Lhouty, D. Tichit, F. Figueras and P.. Geneste, Appl. Catal. A 164 (1997) 251.
[8] K.K. Rao, M. Gravelle, J.S. Valente and F. Figueras, J. Catal. 173 (1998) 115.
[9] D. Tichit and F.. Fajula, Stud. Surf. Sci. Catal. 125 (1999) 329.
[10] M. Del Ario, S. Gutierrez, C. Martin and V.. Rives, Phys. Chem. Chem. Phys. 3 (2001) 119.
[11] P.S. Kumbhar, J. Sanchez-Valente, J. Lopez and F. Figueras, *Chem. Commun.* (1998) 535..
[12] J. Lopez, J. Sanchez-Valente, J.-M. Clacens and F. Figueras, J. Catal. 208 (2002) 30.
[13] C. Lahouse, J. Bachelier, J.C. Lavalley, H. Lauron-Pernot and A.-M. Le Govic, J. Mol. Catal. 87 (1994) 329.
[14] H. Lauron-Pernot, F. Luck and J.M. Popa, Appl. Catal. 78 (1991) 213.
[15] N.E. Fouad, P. Thomasson, P. and H. Knozinger, Appl. Catal. A 194 (2000) 213.
[16] R. Tanner, P. Gill, R.P.K. Wells, J.E.. Bailie, G. Kelly, S.D. Jackson and G.J. Hutchings, Phys. Chem. Chem. Phys. 4 (2002) 688.
[17] G.C. Bond, Catal. Rev. Sci. Eng. 42 (2000) 323.
[18] N. Takezawa and H. Kobayashi Chem. Lett. (1977) 123..
[19] L. Horner and U.B. Kaps, Liebigs Ann. Chem. (1980) 192..
[20] J. Shabtai, R. Lazar and E. Biron, J. Mol. Catal. 27 (1984) 35.
[21] V.A. Ivanov, J. Bachelier, F. Audry and J.C. Lavalley, J. Mol. Catal. 91 (1994) 45.
[22] E.J. Creyghton, S.D. Ganeshie, R.S. Downing and H. Bekkum, J. Mol. Catal. A 115 (1997) 457.
[23] J.C. Waal, K. Tan and H. Bekkum, Catal. Lett. 41 (1996) 63.
[24] J.C. Jansen, E.J. Creyghton, S.L. Njo, H. Koningsveld and H. Bekkum, Catal. Today. 38 (1997) 205.
[25] J.C. Waal, P.J. Kunkeler, K. Tan and H. Bekkum, J. Catal. 173 (1998) 74.
[26] R. Anwander and C. Palm, Stud. Surf. Sci. Catal. 117 (1998) 413.
[27] R.A. Sheldon, Chem. Ind. 75 (1988) 273.
[28] P.J. Kunkeler, B.J. Zuurdeeg, J.C. vander Waal, J.A. Bokhoven, D.C. Koningsberger and H. Bekkum, J. Catal. 180 (1998) 234.
[29] M.A. Aramendia, V. Borau, C. Jimenez, J.M. Marinas, J.R. Ruiz and F.J. Urbano, J. Colloid Interf. Sci. 238 (2001) 385.
[30] A. Corma, M.E. Domine, L. Nemeth and S. Valencia, J. Am. Chem. Soc. 124 (2002) 3194.
[31] M.A. Aramendia, V. Borau, C. Jimenez, J.M. Marinas, J.R. Ruiz and F.J. Urbano, J. Chem. Soc. Perkin 2 (2002) 1122.
[32] E.G. Derouane, C. Dillon, D. Bethell and S.B. Derouane-Abd. Hamid, J. Catal. 187 (1999) 209.
[33] E.G. Derouane, G. Crehan, C.J. Dillon, D.. Bethell, H. He and S.B. Derouane-Abd. Hamid, J. Catal. 194 (2000) 410.