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Use of catalytic reactions to probe Mg–Al mixed oxide surfaces

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In this work, we investigated the effect of catalyst composition on the surface reactivity of magnesium–aluminum mixed oxides using three probe reactions: dehydrogenation of 2-propanol to propanone, dehydration of 2-propanol to propene, and isomerization of 1-butene. Turnover rates were calculated from the total CO_2 adsorption capacity of the mixed oxides, assuming one adsorption site corresponds to one active site. Turnover rates for the dehydrogenation of 2-propanol were independent of the catalyst composition, which is consistent with the structure insensitivity of dehydrogenation reactions. The other two probe reactions followed opposite trends with the Mg : Al ratio: as the Al content of the mixed oxides increased, the turnover rate for 2-propanol dehydration increased while that for 1-butene isomerization decreased. The magnitude of these changes confirms that the mixed oxides are truly interdispersed and not present as separate phases.

Keywords: Magnesia; alumina; hydrotalcite; mixed oxides; 2-propanol dehydration and dehydrogenation; butene isomerization

1. Introduction

In a previous paper [1], we discussed the steady-state reactions of 2-propanol over MgO, Al_2O_3, and Mg–Al mixed oxides derived from hydrotalcites. We argued that the structure sensitivity or insensitivity of alcohol decomposition over oxide powders could not be readily inferred from a comparison of the areal rates over different oxide catalysts. One reason for this conclusion was that Djega-Mariadassou et al. [2] reported that 2-propanol dehydrogenation over oriented ZnO powders was structure insensitive, while Zwicker et al. [3] and Vohs and Barteau [4] found that 2-propanol decomposition on ZnO single crystals was highly dependent on the exposed crystal plane. The single crystal studies demonstrated that exposed metal cations were necessary to form an active site, since an oxygen-terminated ZnO surface was completely inactive for the reaction. In contrast, the oriented powder

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experiments were all performed on surfaces that exposed metal cations and oxygen anions.

A better understanding of the question of the structure sensitivity of reactions on oxide powders could be obtained from a comparison of turnover rates based on metal–oxygen pairs rather than a comparison of areal rates. For a study of catalytic reactions on a single crystal or a well-ordered powder, an estimate of surface sites can be obtained simply by counting exposed pairs on the ideal exposed crystallographic plane. However, this method is not likely to provide an accurate estimate for powdered oxides that expose several different planes. Furthermore, for materials such as Mg–Al mixed oxides there is not yet a definite consensus concerning the surface structure, further complicating estimation of active site densities. Thus, a method of estimating the densities of exposed oxygen–metal pairs by a simple adsorption technique would be useful. Since experiments with ZnO have shown that CO_2 does not adsorb on oxygen-terminated planes [5], we believe that adsorption of CO_2 would serve as such a probe for Mg–Al mixed oxides. In addition, we previously found that the adsorption capacities of MgO, Al_2O_3, and Mg–Al mixed oxides were similar for CO_2 and 2-propanol, as determined by temperature-programmed reaction and desorption [6]. Therefore, in this work, the densities of exposed metal–oxygen pairs on these oxides were estimated by the adsorption of CO_2 and used to re-assess the structure sensitivity or insensitivity of the dehydrogenation of 2-propanol. The surface compositions of the mixed oxides were also probed by the dehydration of 2-propanol, and the isomerization of 1-butene to cis-2-butene and trans-2-butene.

2. Experimental

2.1. SAMPLE PREPARATION

Hydrotalcites, or magnesium–aluminum hydroxycarbonates, are convenient precursors for preparing Mg–Al mixed oxides since magnesium and aluminum are mixed homogeneously throughout the hydroxycarbonate, and the Mg : Al ratio can be varied in a controlled manner. In this work, hydrotalcites were prepared with Mg : Al molar ratios of 5 : 1, 3 : 1, and 2 : 1 by the coprecipitation of aqueous magnesium nitrate and aluminum nitrate with a solution of aqueous potassium hydroxide and potassium carbonate. The synthesis method is described in detail in an earlier paper [1]. In addition to the three samples, hydrotalcite with a Mg : Al ratio of 2 : 1 was synthesized using ammonium carbonate and ammonium hydroxide as the precipitating agents to eliminate any effect of residual alkali on the properties of the mixed oxide. Hereafter, the hydrotalcites are identified by the Mg : Al ratio and the counter ion in the precipitation solution (i.e. HT5 : 1-K, HT2 : 1-NH_4). Magnesium hydroxide and aluminum hydroxide were prepared separately by the addition of aqueous KOH to solutions of $Mg(NO_3)_2$ and

$Al(NO_3)_3$, respectively to allow for direct comparison with the mixed oxide systems.

A standard activation procedure was always performed before any adsorption or reaction. The hydrotalcite or hydroxide sample was heated in situ in flowing He to 823 K at a heating rate of 4 K min^{-1} and calcined for 4 h. Hydrotalcites calcined in this fashion revealed a diffuse MgO X-ray diffraction pattern [1].

2.2. CATALYTIC REACTIONS

The steady-state reaction of 2-propanol was carried out at atmospheric pressure in a single-pass flow system operated at differential conversion ($< 5\%$) [1].

The isomerization of 1-butene was studied using a closed-loop recirculation system with a total volume of 1.2 ℓ. The masses of catalysts were chosen to produce approximately the same total surface area of oxide after in situ calcination. A sample was cooled to room temperature after activation at 823 K, and the entire system was then evacuated to 10^{-5} mbar. Subsequently, 1-butene (Aldrich, 99%) was added, to a pressure of 200 mbar. Since dioxygen is known to rapidly poison the isomerization reaction [7], three freeze–pump–thaw cycles were used to remove any gaseous impurity in the 1-butene. After the butene purification, helium (Roberts Oxygen, 99.999%) was added to bring the total pressure to atmospheric. The 1-butene/He mixture was circulated through the reaction system and 10 µl samples were withdrawn by an in-line sampling valve and analyzed by gas chromatography. The only products detected were cis-2-butene and trans-2-butene.

3. Results

The surface areas and CO_2 adsorption capacities of the oxides are listed in table 1. The BET surface areas were derived from N_2 adsorption and the CO_2 adsorption sites were quantified by temperature-programmed desorption [1].

The results from the steady-state reactions of 2-propanol are presented in

Table 1
CO_2 adsorption capacities of MgO, calcined hydrotalcites, and Al_2O_3 [1]

Sample [a]	Surface area [b] ($m^2 g^{-1}$)	CO_2 adsorption capacity [c] ($10^{-6} mol m^{-2}$)
MgO	200	4.4
HT5 : 1-K	230	2.2
HT3 : 1-K	210	2.9
HT2 : 1-K	230	2.8
HT2 : 1-NH_4	230	2.1
Al_2O_3	290	1.4

[a] Catalysts were calcined at 823 K for 4 h in flowing He.
[b] Determined by N_2 adsorption.
[c] Determined by temperature-programmed desorption of CO_2.

table 2 [1]. The rates of formation of propanone and propene are reported at a common temperature of 593 K.

The dependence of the initial 1-butene isomerization rate on the reactant pressure is shown in fig. 1. The reaction rate at low conversion follows simple first-order kinetics, in accord with the results of other investigators [7–11]. The isomerization results are reported here as initial reaction rates. Butene isomerization was carried out with an initial 1-butene pressure of 200 mbar, a reaction temperature of 340 K, and a total catalyst surface area of approximately 6 m^2. The 1-butene isomerization rates and the cis/trans ratios found at 274, 297, and 340 K are reported in table 3. For each catalyst, the cis/trans ratios decreased as the reaction temperature increased, which is similar to the behavior previously observed over MgO by Baird and Lunsford [7].

4. Discussion

A full comparison of the kinetics results for the reactions of 2-propanol over the mixed oxides is given in our previous paper [1]. Therefore, the focus of the discussion will be on the isomerization of 1-butene.

The isomerization of 1-butene over MgO and Al_2O_3 has been studied previously by several investigators. The initial areal rate at 297 K over MgO ex-hydroxide calcined at 823 K was 7.7×10^{-7} mol m^{-2} s^{-1}, which compares reasonably well with a rate of 6.3×10^{-7} mol m^{-2} s^{-1} found at 299 K over MgO calcined at 773 K [7] and converted to 200 mbar of butene assuming a first-order dependence. The areal rate of isomerization at 297 K over alumina calcined at 823 K is 9.9×10^{-9} mol m^{-2} s^{-1} and compares favorably with literature values of 4×10^{-9} mol m^{-2} s^{-1} at 292 K over alumina calcined at 873 K [12], 2.5×10^{-9} mol m^{-2} s^{-1} at 301 K over alumina calcined at 793 K [13], and 1.8×10^{-9} mol m^{-2} s^{-1} at 296 K over alumina calcined at 823 K [14]. In every case, the areal rate of isomerization over magnesia was two orders of magnitude greater than the rate over alumina at the same conditions.

Table 2
Steady-state reaction rates for the conversion of 2-propanol [a] [1]

Sample [b]	Rate of propanone formation (10^{-9} mol m^{-2} s^{-1})	Rate of propene formation (10^{-9} mol m^{-2} s^{-1})
MgO	11.5	0.36
HT5 : 1-K	7.3	0.47
HT3 : 1-K	6.7	1.28
HT2 : 1-K	7.5	3.21
Al_2O_3	2.7	105

[a] Reactions were performed at 593 K using 500 mbar 2-propanol diluted with 500 mbar He.
[b] Catalysts were calcined at 823 K for 4 h in flowing He.

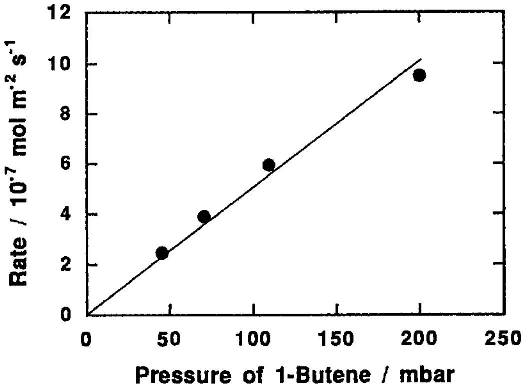

Fig. 1. Dependence of initial reaction rate on 1-butene pressure. Reactions at 340 K over MgO calcined at 823 K for 4 h.

The 1-butene isomerization rates and the cis/trans ratios for calcined HT2 : 1-K and HT2 : 1-NH_4 are essentially the same, indicating that the surface reactivities of the mixed oxides are little affected by any alkali impurities. In addition, the temperature-programmed reactions of 2-propanol on these materials were studied previously [6], and HT2 : 1-K and HT2 : 1-NH_4 exhibited similar selectivities for the reaction products. Therefore, any significant differences in reactivity among the samples can be attributed to variations in the surface structure and composition as the Mg : Al ratios change, rather than differences in the alkali impurity levels.

The activation energies, E_a, for 1-butene isomerization were estimated from the initial rate data at 273, 297, and 340 K, and the values are reported in table 3. The activation energies for isomerization are very low over MgO and the mixed oxides and are similar to the value of 18.8 kJ mol^{-1} found by Baird and Lunsford [7] for MgO.

Table 3
Reaction rates for the isomerization of 1-butene [a]

Sample [b]	Isomerization rate (10^{-7} mol m^{-2} s^{-1})			Cis/trans ratio			E_a (kJ mol^{-1})
	340 K	297 K	274 K	340 K	297 K	274 K	
MgO	9.5	7.7	3.8	3.5	4.9	6.4	10.2
HT5 : 1-K	4.0	3.2	2.2	5.4	7.1	8.8	6.6
HT3 : 1-K	3.0	1.2	1.1	4.1	5.5	7.1	12.3
HT2 : 1-K	2.6	2.1	1.2	3.9	5.5	7.4	8.7
HT2 : 1-NH_4	1.6	–	1.2	3.9	–	7.5	
Al_2O_3	0.099	–	–	2.6	–	–	

[a] Reactions were performed using 200 mbar 1-butene diluted with 800 mbar He.
[b] Catalysts were calcined at 823 K for 4 h in flowing He.

The cis/trans ratios found over all the oxides at all conditions were greater than one, which suggests that the reaction mechanism for the selective production of cis-2-butene is the same as the one proposed by Baird and Lunsford [7] for MgO and by Gerberich and Hall [15] and Medema [9] for Al_2O_3. In this mechanism, the active site for double-bond migration consists of a low-coordination surface oxygen anion and an adjacent pair of metal cations. Since the diameter of an oxide ion (2.64 Å) is slightly smaller than the separation between the terminal carbons of cis-2-butene and the gauche form of 1-butene (2.74 Å), these molecules can drape over the oxide ion and are stabilized by the electrostatic interactions between the terminal carbon atoms and the metal cations. The basic oxide ion aids in removing an allylic proton and transferring it to a terminal methylene group. The stabilization of cis-2-butene during double-bond migration accounts for cis/trans ratios that exceed 1.

As previously noted, we propose to use the amount of CO_2 that adsorbed on an oxide as an estimate of the number of reactive metal–oxygen pairs on the surface. Dividing the rates of the three reactions studied by the CO_2 adsorption capacities of the oxides yields the turnover rates in table 4.

The turnover rates for the formation of propanone from 2-propanol varied by less than a factor of two over the different oxides. This remarkable agreement suggests that the dehydrogenation of 2-propanol is structure-insensitive on all the catalysts studied. Thus, propanone formation requires a simple reaction site, quite probably the same metal–oxygen pairs needed for CO_2 adsorption. Indeed, some mechanisms that have been proposed for secondary alcohol dehydrogenation [16–19] require participation of only one metal cation and an adjacent oxygen anion.

In contrast to the dehydrogenation results, the turnover rates for 2-propanol dehydration increase by three orders of magnitude as the catalyst is changed from magnesia to alumina. Apparently, the surface sites counted by CO_2 TPD do not function equally for alcohol dehydration. This is not unexpected since alcohol

Table 4
Turnover rates over MgO, calcined hydrotalcites, and Al_2O_3

Sample [a]	Turnover rates		
	propanone formation [b] (10^{-3} s^{-1})	propene formation [b] (10^{-4} s^{-1})	1-butene isomerization [c] (s^{-1})
MgO	2.6	0.82	0.22
HT5 : 1-K	3.3	2.1	0.18
HT3 : 1-K	2.3	4.4	0.10
HT2 : 1-K	2.7	11.5	0.093
Al_2O_3	1.9	750	0.0071

[a] Catalysts were calcined for 4 h at 823 K in flowing He.

[b] Reaction temperature was 593 K.

[c] Reaction temperature was 340 K.

dehydration is usually considered an acid-catalyzed reaction and CO_2 is usually used to probe base catalysts. By using Na to poison the reaction of 2-butanol over alumina, Pines and Haag [20] estimated that alumina contains 1.7×10^{-6} mol sites m^{-2} for alcohol dehydration. This value is similar to the site density of 1.4×10^{-6} mol m^{-2} for CO_2 adsorption on alumina found in this work, which suggests that the density of CO_2 adsorption sites constitutes an upper bound for the estimate of reaction site densities. On the less active oxides, the turnover rate depends strongly on the surface composition and the active site densities may be a small fraction of the CO_2 adsorption sites.

A large difference in the reaction rates over alumina and magnesia is not unexpected since the mechanism for secondary alcohol dehydration over basic oxides, such as magnesia [21] differs from the dehydration mechanism over alumina [22,23]. The results of Narayanan et al. [24] show that strongly acidic sites of alumina are poisoned by trace alkali, such as that in our samples. Also, our previous TPR results [6] show that our alumina sample does not possess the very strong acid sites that catalyze low-temperature alcohol dehydration. Thus a comparison of our alumina with magnesia is not unwarranted.

The turnover rate for propene formation over HT2 : 1-K is an order of magnitude larger than that over MgO. A possible explanation for this difference may be found in the work of McCaffrey et al. [25] on the reactions of 2-propanol over alkaline earth oxides. They attributed a larger rate of propene formation on BeO, compared to MgO, to the much lower Lewis base strengths of the oxygen anions of BeO. During dehydration over basic oxides, 2-propanol is believed to undergo β-deprotonation followed by α-protonation [21]. According to McCaffrey et al., as the Lewis basicity increases, the tenacity with which the surface retains protons also increases [25]. Thus, α-protonation is less likely and the dehydration rate decreases.

For the Mg–Al mixed oxides, changes in the surface acidity may also be caused by an inductive effect of the incorporation of aluminum. According to the hypothesis of Tanabe et al. [26], the incorporation of Al into a MgO lattice should enhance both the Lewis acidity of the solid and its reactivity for dehydration. Indeed, we observe an increase in the rate of propene formation with increasing aluminum content. However, some X-ray amorphous aluminum-rich phases may exist in the mixed oxides and could account for the greater dehydration rates.

The turnover rate for the isomerization of 1-butene over MgO is two orders of magnitude larger than the rate of Al_2O_3. One possible reason for the variation in the isomerization rate over the oxides is a change in the number of active sites. The poisoning of 1-butene isomerization with H_2S [10,11], SO_2 [11], and NH_3 [12] produced estimates of $(5.5–8.0) \times 10^{-7}$ mol m^{-2} for the maximum concentration of active sites on alumina. The poisoning of the isomerization of cis-2-butene to 1-butene on MgO ex-hydroxide with CO_2 and H_2O [27] required the adsorption of $(3.0–4.0) \times 10^{-6}$ mol m^{-2}, which is similar to the amount of CO_2 adsorbed on MgO in this work. This suggests that the site for 1-butene isomerization on MgO probably consists of two magnesium cations and one oxygen anion, while on Al_2O_3 additional criteria are required. These criteria could include a specific ensemble of surface atoms, or atoms with low coordination numbers, such as those at ledges or corners. Therefore, the sites for isomerization on the Mg–Al mixed oxides are probably only a fraction of the total CO_2 adsorption sites.

However, the reported differences in the concentrations of active centers do not completely account for the differences in the turnover rates. If the specific reaction rates for butene isomerization in this work are divided by the site concentrations determined from the previously cited poisoning experiments, then the resulting turnover rates range from 0.25 to 0.35 s^{-1} for magnesia and from 0.012 to 0.018 s^{-1} for alumina. Since the turnover rates over MgO and Al_2O_3 still differ by an order of magnitude, there is probably an effect of the acid and base character of the oxides on the absolute reaction rate. Interestingly, work by Gerberich and Hall [15] suggests that the Lewis acidity of the metal cations, rather than the basicity of the oxygen anions, may be an important factor. For example, they reported that the reaction rate over alumina doubled when 1.22 wt% fluorine was incorporated, displacing hydroxide. They attributed this change to enhanced electropositivity for the aluminum ions. Similarly, the electronegativity of Mg (1.2) is less than that of Al (1.5), which may account for the remaining differences in the 1-butene turnover rates.

The reactions studied also provide evidence that the calcined hydrotalcites produce fairly homogeneous mixed oxides rather than a physical mixture of magnesia and alumina. On a physical mixture of magnesia and alumina with a Mg : Al atomic ratio of 3 : 1, the turnover rate for 2-propanol dehydration was $110 \times 10^{-4}\ s^{-1}$ [1]. This is similar to the value of $190 \times 10^{-4}\ s^{-1}$ calculated as a weighted average of the turnover rates of Al_2O_3 and MgO, and is approximately two orders of magnitude greater than the turnover rate of $4.4 \times 10^{-4}\ s^{-1}$ found on HT3 : 1-K. The mixed oxides prepared from hydrotalcites clearly exhibit different surface reactivities than a physical mixture does.

5. Conclusions

The adsorption of CO_2 is a simple and useful technique for estimating the concentrations of exposed metal–oxygen pairs on a basic oxide powder. A comparison of turnover rates based on the CO_2 adsorption capacities provided a better understanding of the mixed oxide surfaces than did a comparison of reaction rates normalized by specific surface areas. For the materials in this study, the dehydrogenation of 2-propanol to propanone is insensitive to the composition of the surface. In contrast, the dehydration of 2-propanol to propene and the isomerization of 1-butene are both strongly affected by the alumina content of the material. As the Mg : Al ratios of the mixed oxides increased, the turnover rate for propene formation increased and that of 1-butene isomerization decreased. A comparison of reaction rates indicates that the calcined hydrotalcites form well-mixed oxides instead of physical mixtures of separate phases.

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References

[1] A.L. McKenzie, C.T. Fishel and R.J. Davis, J. Catal. 138 (1992) 547.
[2] G. Djega-Mariadassou, L. Davignon and A.R. Marques, J. Chem. Soc. Faraday Trans. I 78 (1982) 2447.
[3] G. Zwicker, K. Jacobi and J. Cunningham, Int. J. Mass Spectrom. Ion Processes 60 (1984) 213.
[4] J.M. Vohs and M.A. Barteau, J. Phys. Chem. 95 (1991) 297.
[5] S. Akhter, K. Lui and H.H. Kung, J. Phys. Chem. 89 (1985) 1958.
[6] C.T. Fishel and R.J. Davis, Langmuir, in press.
[7] M.J. Baird and J.H. Lunsford, J. Catal. 26 (1972) 440.
[8] J.W. Hightower and W.K. Hall, J. Phys. Chem. 71 (1971) 1014.
[9] J. Medema, J. Catal. 37 (1975) 91.
[10] J.H. Lunsford, L.W. Zingery and M.P. Rosynek, J. Catal. 38 (1975) 179.
[11] M.P. Rosynek and F.L. Strey, J. Catal. 41 (1976) 312.
[12] Y. Amenomiya, J. Catal. 46 (1977) 326.
[13] M.P. Rosynek, W.D. Smith and J.W. Hightower, J. Catal. 23 (1971) 204.
[14] A. Ayame and G. Sawada, Bull. Chem. Soc. Japan 62 (1989) 3055.
[15] H.R. Gerberich and W.K. Hall, J. Catal. 5 (1966) 99.
[16] O. Koga, O. Takaharu and K. Tamaru, J. Chem. Soc. Faraday Trans. I 76 (1980) 19.
[17] E. Akiba, M. Soma, T. Onishi and K. Tamaru, Z. Phys. Chem. NF 119 (1980) 103.
[18] M. Bowker, R. Petts and K. Waugh, J. Chem. Soc. Faraday Trans. I 81 (1985) 3073.
[19] D. Chadwick and P.J.R. O'Malley, J. Chem. Soc. Faraday Trans. I 83 (1987) 2227.
[20] H. Pines and W.O. Haag, J. Am. Chem. Soc. 82 (1960) 2471.
[21] T.J. Mazanec, J. Catal. 98 (1986) 115.
[22] H. Pines and J. Manassen, Adv. Catal. 16 (1966) 49.
[23] T. Yamaguchi and K. Tanabe, Bull. Chem. Soc. Japan 47 (1974) 424.
[24] C.R. Narayanan, S. Srinivasan, A.K. Datye, R. Gorte and A. Biaglow, J. Catal. 41 (1976) 312.
[25] E.F. McCaffrey, T.A. Micka and R.A. Ross, J. Phys. Chem. 76 (1972) 3372.
[26] K. Tanabe, T. Sumiyoshi, K. Shibata, T. Kiyoura and J. Kitagawa, J. Bull. Chem. Soc. Japan 47 (1974) 1064.
[27] J.L. Lemberton, G. Perot and M. Guisnet, J. Catal. 89 (1984) 69.