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The Selectivity of Sodium Carbonate-Doped Zinc Phosphate in the Gas-Phase Dehydrogenation–Dehydration of Cyclohexanol

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In this work, $Zn_3(PO_4)_2$ (solid ZnP) was synthesized by precipitation from an aqueous solution containing $ZnCl_2$ and Na_2HPO_4. A zinc oxide was also synthesized under the same conditions by precipitation from aqueous $ZnCl_2$. Addition of Na_2CO_3 to the medium and heating at 323–343 K for 6 h gave rise to $NaZnPO_4$ (solid NaZnP) and ZnO, respectively, both of which were found to exhibit excellent activity in the dehydrogenation of cyclohexanol. XRD and IR analyses revealed amorphous Na_2CO_3 to be deposited on the solid surface, as well as the potential presence of residual zinc oxides resulting from decomposition of the $ZnCO_3$ formed. The presence of Na_2CO_3 on the solid surface increases its basicity and inhibits dehydration of cyclohexanol. At 773 K, $Zn_3(PO_4)_2$ yields cyclohexene and cyclohexanone, whereas, under the same reaction conditions, $NaZnPO_4$ produces the ketone selectively.

INTRODUCTION

Probably over one-half of all chemical products are obtained by selective oxidation reactions (1), in many of which catalysis plays active role. One essential objective in addressing an oxidation process is to avoid the formation of by-products impurifying the reaction mixture. Alcohol oxidation is an extremely interesting process which has been thoroughly studied under the effect of both homogeneous and heterogeneous catalysis (2). Alcohols can be oxidized to carbonyl compounds (aldehydes and ketones) or carboxylic acids. There are a number of available procedures for selective oxidation of alcohols that provide good results in a homogeneous phase but demand very strict control of the reaction conditions (2). The catalyst has a decisive influence on the selectivity achieved in oxidation reactions subject to heterogeneous catalysis. In many processes, a primary alcohol is converted into an aldehyde and a secondary alcohol into a ketone in the gas phase by using a catalyst consisting of a metal oxide such as MgO (3), ZnO (4–6), FeO (7, 8), and Cr_2O_3 (9), or an oxide mixture such as NiO–CuO (10), among others.

The dehydrogenation reaction involved in alcohol oxidation usually competes with dehydration of the starting compound to an olefin, which is produced in a variable proportion depending on the particular catalyst and reaction conditions. The selectivity exhibited by a catalyst is related to its surface acid–base and redox properties (11–14). Such properties are acquired during its synthesis. Many authors ascribe the dehydrating activity of oxides to their Brønsted surface acidity, involved in E_1 mechanisms (via carbenium ions), or acid–base pairs acting via an E_2 (via uncharged intermediate species) or E_{1cb} (via carbanions) mechanism (15). On the other hand, the dehydrogenation reaction appears to be related to the catalyst's surface basicity (16, 17).

A variety of orthophosphates including $AlPO_4$ (18–21), $BiPO_4$ (22, 23), BPO_4 (24), $FePO_4$ (25), Li_3PO_4 (26, 27), $Zn_3(PO_4)_2$ (28), and $Zr_3(PO_4)_2$, among others (19), have also been used in various organic syntheses. Of these, calcium orthophosphate (hydroxyapatite) (30) and zinc orthophosphate (28) are reportedly active in the dehydrogenation of primary and secondary alcohols. In the presence of hydroxyapatite in a stoichiometric ratio ($P/Ca = 0.6$), the rate of alcohol decomposition is zero-order in the dehydration and dehydrogenation; at higher ratios (e.g., $P/Ca = 0.63$), however, only dehydration takes place.

Zinc orthophosphate [$Zn_3(PO_3)_2$] was used for the dehydrogenation and dehydration of 2-butanol between 623 and 923 K. Increasing the reaction temperature for this solid from 573 to 923 K resulted in increasing dehydrogenating activity, which reflected in the preferential production of 2-butanone. On the other hand, the dehydrating activity and the amount of butenes produced decreased under the same conditions (28).

Some solids containing SiO_2, Al_2O_3, Cr_2O_3, and MgO have also been prepared from various nitrates and carbonates as doping agents (31–34) that exhibit variable activity in different organic processes. The synthetic procedure used at our laboratory provides highly active, extremely selective catalysts for the dehydrogenation of cyclohexanol.

This work reports on the structure and the textural and

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surface acidity properties of new $NaZnPO_4$ catalysts that were synthesized here for the first time and doped with Na_2CO_3 during their synthesis. The catalysts exhibit excellent selectivity towards the gas-phase conversion of cyclohexanol into cyclohexanone at 623–773 K.

EXPERIMENTAL

Catalyst Synthesis

3 *N* NaOH was added dropwise to an aqueous solution containing 155.5 g of $ZnCl_2$ and 115 g of Na_2HPO_4 up to pH 9. The precipitate thus formed was allowed to stand and was then filtered and air dried in order to obtain a solid called ZnP. The solid (25 g) was then suspended in 200 ml of water at 343 K and 100 ml of saturated Na_2CO_3 solution was added dropwise. The solid resulting after 24 h standing, NaZnP, was filtered and air dried. Finally, each solid was calcined stepwise according to the following temperature programme: 1 h at 473 K, 1 h at 573 K, 1 h at 673 K, and 1 h at 773 K.

Solid ZnO was also synthesized by following the above-described procedure, but without adding Na_2HPO_4 to the reaction medium.

Finally, solid ZnO_C was commercially available zinc hydroxide (Probus ref. 50286, puriss. grade) that was calcined by the same procedure as all the other solids prior to reaction.

All solids were sifted through 200–250 mesh.

Chemical and Textural Properties of the Catalysts

The specific surface area of the synthesized solids was determined by using the BET method on a Micromeritics ASAP 2000 analyzer.

Acid and basic sites were quantified from the retention isotherms of two different titrants (viz. cyclohexylamine for acid sites and phenol for basic sites) dissolved in cyclohexane. The amount of titrant retained by each solid was determined spectrophotometrically. Application of the Langmuir equation provided the amount of titrant adsorbed in monolayer form, X_m, as a measure of acid and basic sites (35).

X-Ray Diffraction Analysis

X-ray powder diffraction patterns were recorded on a Siemens D 500 diffractometer using Cu$K\alpha$ radiation. Scans were performed between $2\theta = 10°$ and $2\theta = 65°$.

IR Spectra

Diffuse reflectance IR spectra for the synthesized solids were recorded from 400 to 6000 cm^{-1} on a Bomen MB-100 FTIR spectrophotometer. Samples were prepared by mixing 0.14 g of powdered solid with KBr (blank) in a 15 : 85 proportion. All samples were previously heated at 573 K in order to remove water.

Reactor

Reactions were carried out in a glass tubular reactor of 20 mm ID that was fed at the top with cyclohexanol by means of a SAGE 35 propulsion pump whose flow rate was controlled via a nitrogen flow meter. The reactor was loaded with 4 g of catalyst, over which 5 g of glass beads acting as a vaporizing layer was placed. The temperature was controlled via an externally wrapped heating wire that covered the height of both the catalytic bed and the vaporizer, and was connected to a temperature regulator. The reactor outlet gases were passed through a condenser and onto a collector that allowed liquids to be withdrawn at different times.

No diffusion control mechanism was detected, nor were any of the reactor elements found to contribute to the catalytic effect under the reactor working conditions (feeding rate = 0.15–60 ml/min; T = 473–823 K; N_2 flow rate = 100 ml/min; amount of catalyst = 2–5 g) in blank runs.

The collected samples were analysed by gas chromatography on a 2-m × $\frac{1}{8}$-in ID column packed with Carbowax over Chromosorb P-10% CW 20 M, using a linear temperature programme (from 333 to 423 K at 30 K/min). The products thus obtained were identified by comparison with standards and their structures confirmed by mass spectrometry.

RESULTS AND DISCUSSION

Structural Analysis

Figure 1 shows the X-ray diffraction patters for the synthesized catalysts calcined at 773 K. A comparison of the bands observed with those listed in ASTM tables allowed the following structures to be established for the solids:

—Solid ZnP673: $Zn_3(PO_4)_2$ (2θ = 28.84°, 24.49°, 28.21°, 22.33°, 21.00°, 19.19°, 36.55°).

—Solid NaZnP673: $NaZnPO_4$ (2θ = 35.45°, 20.21°, 30.31°, 22.25°, 37.24°, 42.80°).

—Solid ZnO673: ZnO, zincite phase.

X-ray diffraction patterns were also recorded for the solids at different temperatures; they revealed a variety of behaviours and transformations depending on the particular solid. Thus, calcination of solid NaZnP between 673 and 773 K revealed sodium zinc phosphate to predominate throughout the temperature range. On the other hand, solid ZnP was found to consist of zinc phosphate at 673 K and a complex structure [possibly $Na_9Zn_{21}(PO_4)_{17}$] at 773 K that remained unaltered after that. At no time was any signal for intermediate alkaline chlorocar-

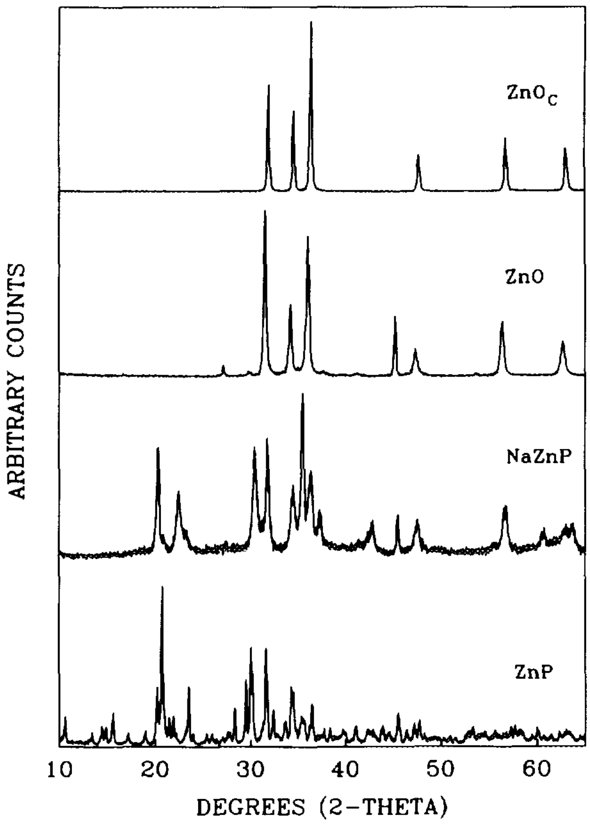

FIG. 1. X-ray diffraction patterns obtained for the synthesized solids calcined at 773 K.

bonates similar to the aluminium and potassium hydroxycarbonates observed by Montagne *et al.* (34) or Tomilov and co-workers (36, 37) on depositing K_2CO_3 over γ-alumina detected.

The bands at $2\theta = 31.70°$, $45.44°$, $27.16°$, and $66.12°$ for solid NaZnP673 were assigned to NaCl formed during the synthesis, while those at $2\theta = 31.53°$, $20.21°$, $67.86°$, and $56.44°$ were assigned to zincite ZnO resulting from decomposition of $ZnCO_3$ ($K_S = 1.19 \times 10^{-10}$) or $Zn(OH)_2$ ($K_S = 4.12 \times 10^{-17}$), both of which were formed in the process. Addition of Na_2CO_3 during the synthesis may have given rise to insoluble $ZnCO_3$, which would have decomposed to ZnO and CO_2 at 724 K. On the other hand, no residual crystalline, natrite-type or gregoryite-type Na_2CO_3 was detected.

Solids ZnO and ZnO_C occurred both as zincite throughout the temperature range studied. The differences between the X-ray diffraction patterns for the two solids lay in the NaCl present in ZnO, which was absent from its commercially available counterpart (ZnO_C). The bands at $2\theta = 34.1°$ and $36.0°$ were assigned to residual Na_2HPO_4 species potentially remaining after the catalyst synthesis.

Textural and Surface Acid–Base Properties

Table 1 summarizes the textural properties of the synthesized solids calcined at various temperatures. As can be seen, all synthesized solids had a small specific surface area that generally decreased with increasing calcination temperature. The zinc oxides had somewhat larger specific surface areas than did the orthophosphates ZnP and NaZnP. The average pore diameter for the solids ranged from 250 to 310 Å.

The solids exhibited virtually no acidity (< 0.1 μmol/g) against cyclohexylamine dissolved in cyclohexane, so they could not be titrated in this way. The basicity of the catalysts calcined at 673 K, as measured by spectrophotometric titration with phenol dissolved in cyclohexane, was 1.5 μmol/g (ZnP), 5.2 μmol/g (NaZnP), 14.1 μmol/g (ZnO), and 4.0 μmol/g (ZnO_C), respectively. Therefore, the solids possess a predominant population of basic sites, which, however, is much smaller than that of a typical aluminium (166 μmol/g) (39) or magnesium orthophosphate (9.4 μmol/g) (40)—except ZnO—obtained under similar conditions.

We recorded the diffuse reflectance IR spectra for the solids calcined at 773 K; those for the solids calcined at 673 K were also obtained, but were very similar to the previous ones, so only the former are discussed. Thus, Fig. 2 shows the spectra for the solids calcined at 773 K and compares those for Na_2CO_3 (Panreac ref. 141648) and Na_2HPO_4 (Panreac ref. 141679) calcined at the same temperature. None of the solids studied exhibited IR absorption over the range 4000–6000 cm^{-1}. Because spectra were recorded for samples heated at 573 K, the solids showed a band at 3530 cm^{-1} corresponding to a small population of surface hydroxyl groups. In common with Na_2HPO_4, solids ZnP773 and NaZnP773 exhibited a band multiplet between 1983 and 2114 cm^{-1}, which, however, was somewhat shifted (2002–2245 cm^{-1}) in the spectrum of the latter. On the other hand, there were marked differences between the three solids in the region of 482–1130 cm^{-1}. The bands at 1439 and 1582 cm^{-1} are usually assigned to $P = O$ vibrations (41), while those between 900 and 1200 cm^{-1} are ascribed to ν_{P-O} and those between

TABLE 1

BET Specific Surface Areas (m^2 g^{-1}) of the Synthesized Catalysts at Various Temperatures

	Catalyst			
T_{calc} (K)	ZnP	NaZnP	ZnO	ZnO_C
673	2.6	3.4	8.7	—
723	1.8	3.6	8.0	—
773	1.1	2.6	8.1	2.2

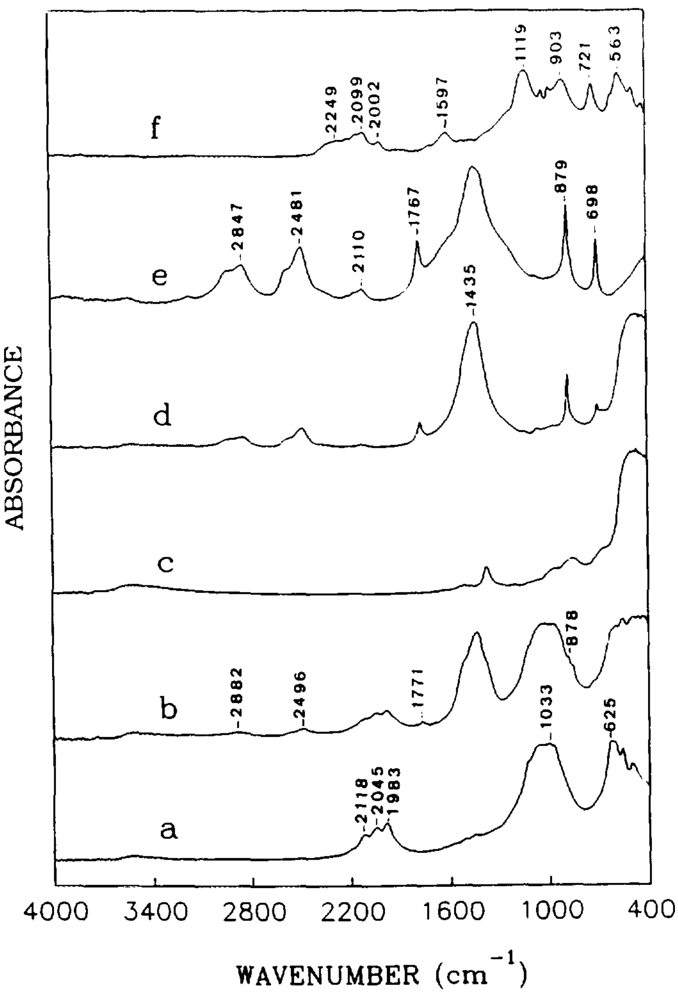

FIG. 2. Diffuse reflectance IR spectra recorded at 573 K for (a) ZnP, (b) NaZnP, (c) ZnO_C, (d) ZnO, (e) Na_2CO_3, and (f) Na_2HPO_4. All samples were calcined at 773 K.

350 and 600 cm^{-1} are assigned to ν_{O-P-O} (41, 42). The strongest bands in the Na_2HPO_4 spectrum (ν_{P-O} = 1130 cm^{-1}) seemingly appeared as a shoulder of the broad band with an absorption maximum at 1041 cm^{-1} in the spectrum for NaZnP773. The most characteristic bands in the Na_2CO_3 spectrum are two of stretching vibrations, viz. ν_{C-O} (1435 cm^{-1}) and $\nu_{C=O}$ (1767 cm^{-1}) (43), others of out-of-plane bending (ν = 879 cm^{-1}), and another three, still unassigned vibrations, at 2481, 2932, and 2847 cm^{-1}. All these bands appeared in the spectra for the solids to which Na_2CO_3 was added during the synthetic process, i.e., NaZnP and ZnO, but not in ZnP or ZnO_C. Therefore, both NaZnP (consisting of $NaZnPO_4$) and ZnO (zinc oxide) seemingly contain surface Na_2CO_3.

The synthetic procedure used (the Na_2CO_3 was added after the orthophosphate was precipitated) allows one to assume that the sodium carbonate present in the final solids accumulated preferentially at the surface. In addition, because it was amorphous, it did not appear anywhere in the X-ray diffraction patterns.

Neither X-ray diffraction nor IR spectroscopy revealed the presence of other species similar to $NaHCO_3$ at the solid surfaces. While some surface ZnO resulting from decomposition of $ZnCO_3$ at the calcination temperature (773 K) might be present, the absorption bands of phosphates and carbonates in the region 1350–1500 cm^{-1} masked the band at 1377 cm^{-1}, characteristic of pure ZnO, so no final conclusion can be drawn in this respect.

Catalytic Activity

The synthesized solids were tested in the gas-phase dehydration–dehydrogenation of cyclohexanol. Reactions were carried out under conditions involving no reactant or product diffusion in accordance with the criteria put forward by Koros and Novak (44). The catalysts were used at a temperature equal to or lower than their calcination temperature in every case.

Figure 3 shows the cyclohexanone (CHONE) conversions provided by catalyst NaZnP at different space times. As can be seen, CHONE conversion decreased with increasing reaction time. The decrease was seemingly linear at all W/F ratios assayed, which suggests that the catalyst is deactivated as a result of the thermal decomposition of cyclohexanol and cyclohexanone to carbon, or the presence of surface oligomers resulting from polycondensation of cyclohexanone, as suggested by Lin and Wang (45).

Very often, olefins are ascribed a high capacity for deactivating catalysts on account of the ease with which they can give rise to surface carbon deposits. However,

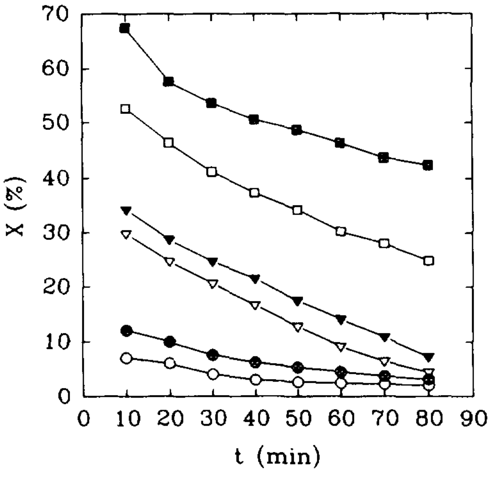

FIG. 3. Variation of cyclohexanone conversion as a function of the reaction time. T_{reac} = 623 K; catalyst, NaZnP673; cyclohexanol feed rate = 0.47 ml/min: N_2 flow rate = 100 ml/min; W/F (feed mol^{-1} h g_{cat}) = 1.8 (○), 3.7 (●), 5.5 (▽), 7.4 (▼), 14.7 (□), and 22.1 (■).

TABLE 2

Overall Conversion, Selectivity to Cyclohexanone, and Specific Catalytic Activity (r_a) Achieved by Using the Synthesized Catalysts at Various Reaction Temperatures

Catalyst	T_{calc} (K)	T_{reac} (K)	X_{TOTAL} (mol%)	S_{CHONE}	$r_a(\times 10^3)$ (mol · h^{-1} m^{-2})
ZnP	673	623	19.9	0.62	5.2
	673	673	23.2	0.60	6.0
	723	723	71.8	0.86	27.0
NaZnP	673	623	24.9	1.00	5.0
	673	673	55.1	1.00	11.0
	723	723	92.9	0.99	17.5
	773	623	29.3	1.00	7.6
	773	773	99.5	0.99	25.9
ZnO	673	623	46.3	1.00	3.6
	673	673	73.2	1.00	5.7
	723	723	80.7	1.00	6.8
	773	773	94.9	0.99	7.9
ZnO_C	773	623	25.6	0.99	7.9

Note. Reaction conditions: W/F (feed mol^{-1} h g_{cat}) = 14.75; N_2 flow rate = 100 ml/min; amount of catalyst = 4 g; $t_{reaction}$ = 80 min; S_{CHONE} = X_{CHONE}/X_{TOTAL}.

our experiments with the catalysts revealed the presence of no cyclohexene or any other olefin among the reaction products. The curves obtained at higher reaction temperatures were similar, but the conversions were higher throughout the range studied. Qualitatively, carbonation was also observed to increase with increase in the reaction temperature.

Table 2 gives the results obtained in the dehydration–dehydrogenation of cyclohexanol at various temperatures. Only catalyst ZnP, consisting of zinc orthophosphate, was found to yield cyclohexene and cyclohexanone. All other catalysts yielded cyclohexanone selectively at any reaction temperature above 623 K. In many instances, the optimal activity and selectivity were achieved by using the catalyst at a reaction temperature identical with its calcination temperature. In fact, reaction temperatures below the corresponding calcination temperatures resulted in much lower yields. While the results varied with the reaction temperature, catalyst NaZnP provided the highest cyclohexanone yields at 723 K.

The X-ray diffraction patterns for the solids ZnP, NaZnP, and ZnO showed the presence of NaCl formed during the synthetic process. We synthesized a zinc orthophosphate from $ZnCl_2$ and H_3PO_4 by using a similar procedure and precipitation with NH_4OH. Unlike the previous ones, it was found to contain no NaCl. Also, it only yielded cyclohexene at 623 K under the same reaction conditions as the previous catalysts. Therefore, the presence of Na^+, Cl^-, and CO_3^{2-} ions seemingly promotes some dehydrogenating activity in the catalysts. Several authors (34) who deposited lithium, sodium, and potassium nitrates and carbonates over SiO_2, Al_2O_3, and Cr_2O_3 observed the presence of surface alkaline silicate, aluminate, or chromate species on calcination between 773 and 1173 K, apparently originating in an acid–base reaction between the alkaline oxide (a base) resulting from decomposition of the corresponding nitrate or carbonate, and a surface acid site. The reactivity of these solids therefore arises from the presence of such species, which form surface agglomerates via the so-called "cement effect" (31). In Na^+-doped alumina, an increase in the amount of surface sodium was found to decrease the acidity and hence production of styrene (the dehydration product) from gaseous benzyl alcohol yielding dibenzyl ether predominantly (32). Su *et al.* (46) recently reported on the activity of an Na_2CO_3 solid prepared by air calcination of $NaHCO_3$ at 523 K in the conversion of methanol to formaldehyde. The sodium carbonate proved active in a disproportionation reaction of methanol since the formaldehyde expected was accompanied by methane and carbon monoxide as reaction products. The activity properties of impregnated Na_2CO_3 over $NaZnPO_4$ or ZnO are not the same as those of the above-mentioned sodium carbonate since at no time did we detect cyclohexene or any other lower or higher hydrocarbon among the reaction products. A cyclohexanol dehydrogenation–dehydration experiment involving pure Na_2CO_3 that was calcined at 773 K for 3 h and the same reaction conditions used with the synthesized solids at 773 K for 80 min showed the overall conversion (CHE + CHONE) obtained to be less than 1%. Deposited sodium carbonate acts by promoting the dehydrogenation of cyclohexanol to cyclohexanone. In fact, sodium carbonate deposited over $Zn_3(PO_4)$, which produces both cyclohexene and cyclohexanone from cyclohexanol, inhibited the dehydration reaction. On the other hand, Na_2CO_3 deposited over ZnO enhanced its dehydrogenating capacity. In both cases, addition of the carbonate increased the number of surface basis sites (47).

Further information, however, is required in order to accurately describe the surface reaction involved. X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray analysis (EDAX) tests are currently being performed in our laboratory in order to determine the proportion of various surface species (Na^+, CO_3^{2-}, Zn^{2+}, and PO_4^{3-}) and elucidate their roles in the activity of the synthesized catalysts.

CONCLUSIONS

We synthesized a $Zn_3(PO_4)_2$ solid that was found to be active in the gas-phase dehydration–dehydrogenation of cyclohexanol. Addition of Na_2CO_3 to the reaction medium produced $NaZnPO_4$ impregnated with residual sodium carbonate at the surface. The solid, which is reported for the first time, exhibited excellent activity in the dehydrogenation of cyclohexanol at 623 K, which is a substantially lower temperature than those typically required by other magnesium and sodium orthophosphates (40) in order to achieve the same conversion and selectivity levels. A zinc oxide synthesized in a similar way as the sodium and zinc orthophosphate but in the absence of sodium dihydrogen phosphate was found to exhibit a higher catalytic activity than did a commercially available zinc oxide. The selectivity of the synthesized catalysts towards cyclohexanone is surprisingly high. In both cases, addition of Na_2CO_3 during the synthetic procedure was found to increase the surface basicity of the solids obtained.

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REFERENCES

1. Tovrog, S., Mares, F., and Diamond, S., "Catalysis of Organic Reactions." Dekker, New York, 1981.
2. Hudlicky, M., "Oxidations in Organic Chemistry," ACS Monograph 186. Am. Chem. Soc., Washington, DC, 1990.
3. Stobbe, D. E., Buren, F. R., Groenendijk, P. E., Dillen, A. J., and Geus, J. W., *J. Mater. Chem.* **1,** 539 (1991).
4. Tsuchida, T., and Kitajima, S., *Chem. Lett.*, 1769 (1990).
5. Hino, M., and Arata, K., *Chem. Lett.*, 1737 (1990).
6. Haile, S. M., and Johnson, D. W. Jr., *J. Am. Ceram. Soc.* **72,** 2004 (1989).
7. Mazanec, T. J., *J. Catal.* **98,** 115 (1986).
8. Sreerama, M., Patnaik, P., Sidneswaran, P., and Jayamani, M., *J. Catal.* **109,** 298 (1988).
9. Nondek, L., Mihajlova, D., Andreev, A., Palazov, A., Kraus, M., and Shopov, D., *J. Catal.* **40,** 46 (1975).
10. Paal, Z., Peter, A., and Tetenyi, P., *React. Kinet. Catal. Lett.* **1,** 121 (1974).
11. Tanabe, K., Misono, M., Ono, I., and Hattori, N., *Stud. Surf. Sci. Catal.*, 51 (1989).
12. Winterbottom, J. M. *in* "Catalysis," Vol. 4, p. 141. Royal Soc. Chem., London, 1981.
13. Ai, M., *J. Catal.* **49,** 305 (1977).
14. Ouqour, A., Coudurier, G., and Vedrine, J. C., *J. Chem. Soc., Faraday Trans.* **89,** 3151 (1993).
15. Figueras-Rocca, F., Mourgues, L., and Trambouze, Y., *J. Catal.* **14,** 107 (1969).
16. Matsumura, Y., Hashimoto, K., and Yoshida, S., *J. Catal.* **117,** 135 (1989).
17. Tomke, K., *Z. Phys. Chem. N. F.* **106,** 225 (1977).
18. Campelo, J. M., García, A., Luna, D., and Marinas, J. M., *J. Catal.* **111,** 106 (1988).
19. Moffat, J. B., *in* "Topics in Phosphorous Chemistry" (M. Grayson and E. J. Griffith, Eds.), Vol. 10, p. 285. Wiley, New York, 1980.
20. Campelo, J. M., García, A., Luna, D., Marinas, J. M., *J. Catal.* **102,** 299 (1986).
21. Peri, J. B., *Discuss Faraday Soc.* **52,** 55 (1971).
22. Sakamoto, T., Egashira, M., and Seiyama, T., *J. Catal.* **16,** 407 (1970).
23. Seiyama, T., Egashira, M., Sakamoto, T., and Aso, I., *J. Catal.* **24,** 76 (1972).
24. Moffat, J. B., and Neeleman, J. F., *J. Catal.* **31,** 274 (1973).
25. Giorgini, M., Bartolozzi, M., F. Morelli, and Di Manno, A., *Ann. Chim. (Rome)* **65,** 29 (1975).
26. Coudurier, M., Mathieu, M. V., Prettre, M., Imelik, B., and Degeorges, M. E., *Bull. Soc. Chim. Fr.*, 1821 (1968).
27. Delgado, A. M., and Sinisterra, J. V., *React. Kinet. Catal. Lett.* **47,** 293 (1992).
28. Tada, A., Itoh, H., Kawasaki, J. M., and Nara, J., *Chem. Lett.*, 517 (1975).
29. Clearfield, A., and Kalnins, J. N., *J. Inorg. Nucl. Chem.* **38,** 849 (1976).
30. Kibby, C. L., and Hall, W. K., *J. Catal.* **31,** 65 (1973); **29,** 144 (1973).
31. Perrichon, V., and Durupty, M. C., *Appl. Catal.* **42,** 217 (1988).
32. Ganesan, K., and Pillai, C. N., *J. Catal.* **119,** 8 (1989).
33. Ramana, D. V., and Pillai, C. N., *Can. J. Chem.* **47,** 3705 (1969).
34. Montagne, X., Durnad, C., and Mabilon, G., *in* "Catalysis by Acids and Bases" (B. Imelik, C. Naccache, G. Coudurier, Y. Ben Taarit, and J. C. Vedrine, Eds.), p. 33. Elsevier, Amsterdam, 1985.
35. Aramendía, M. A., Borau, V., Jiménez, C., Marinas, J. M., and Rodero, F., *Colloids Surf.* **12,** 227 (1984).
36. Tomilov, N. P., Berger, A. S., and Boikova, A. I., *Russ. J. Inorg. Chem. (Engl. Transl.)* **14,** 352 (1969).
37. Berger, A. S., Tomilov, N. P., and Vorsina, I. A., *Russ. J. Inorg. Chem. (Engl. Transl.)* **16,** 42 (1971).
38. "Handbood of Chemistry and Physics," 68th ed., CRC Press, Boca Raton, FL, 1987.
39. Campelo, J. M., García, A., Luna, D., Marinas, J. M., and Moreno M. S., *Bull. Soc. Chim. Fr.* **2,** 283 (1988).
40. Aramendía, M. A., Barrios, J., Borau, V., Jiménez, C., Marinas, J. M., Romero, F. J., Ruiz, J. R., and Urbano, F. J., *in* "Proceedings of the II World Congress & IV European Workshop Meeting, New Developments in Selective Oxidation" (V. Cortés and S. Vic. Eds.). Benalmádena, Spain, 1993.
41. Farmer, U. C. (Eds.), *in* "The Infrared Spectra of Minerals." London, 1974.
42. Campelo, J. M., Marinas, J. M., Mendioroz, S., and Pajares, J., *J. Catal.* **101,** 484 (1986).
43. Nakamoto, K., "Infrared and Raman Spectra of Inorganic and Coordination Compounds," 2nd ed. Wiley, New York, 1978.
44. Koros, R. M. and Novak, E. J., *Chem. Eng. Sci.* **22,** 470 (1967).
45. Lin, Y.-M., and Wang, I., *Appl. Catal.* **41,** 53 (1988).
46. Su, S., Prairie, M. R., and Renken, A., *Appl. Catal.* **91,** 131 (1992).
47. Malinowski, S., *in* "Catalysis by Acids and Bases" Imelik *et al.*, Eds.), Vol. 20, p. 57. Elsevier, Amsterdam, 1985.