Journal of Catalysis **185,** 506–512 (1999)
Article ID jcat.1999.2542, available online at http://www.idealibrary.com on IDEAL®

High Activity Solid Super Base Catalysts Employing Nanocrystals of Metal Oxides: Isomerization and Alkylation Catalysis, Including Conversion of Propylene-Ethylene Mixtures to Pentenes and Heptenes

Naijian Sun and Kenneth J. Klabunde[1]

Department of Chemistry, Kansas State University, Manhattan, Kansas 66506

Received January 27, 1999; revised April 26, 1999; accepted April 30, 1999

Nanocrystalline MgO doped with potassium metal caused the formation of highly basic sites that are capable of alkene isomerization and alkene alkylation, including the conversion of propylene–ethylene mixtures to pentenes and heptenes.

The total number of basic sites closely correlates with the estimated number of ions that exist on edges/corners on the polyhedral crystallites. Only a fraction of these sites are basic enough to cause the alkylation reactions, and these were formed more prevalently on nanocrystalline MgO as compared with microcrystalline MgO. The results represent another example of nanocrystalline materials possessing unique surface chemistry. © 1999 Academic Press

INTRODUCTION

Solid super bases are created when some metal oxides are treated with alkali metals; for example, Na–Al_2O_3 or K–MgO. These materials are highly active catalysts for isomerization of alkenes, even at room temperature (1–3). Successive treatment of Al_2O_3 with NaOH and Na metal allowed Suzukamo to prepare catalysts that were active for side-chain alkylation of alkylbenzenes as well as for isomerization of alkenes (4, 5).

Generally it is believed that very strong base sites are created at surface vacancy sites or other defects that trap excess electron density due to the presence of the alkali metal dopant (1).

Nanoscale materials have generated a great deal of interest in recent years due to their unusual magnetic, optical, physical, and surface chemical properties (6–9). Simple metal oxides such as MgO or CaO possess huge surface areas in nanocrystalline form as well as unusual morphologies that allow them to possess high proportions of edge, corner, and other surface defect sites, which are then intrinsically more surface chemically active (9). These special properties enable such materials to be highly effective adsorbents for acid gases as well as destructive adsorbents for a variety of unwanted chemicals (9, 12, 13). In addition, promising catalytic properties have been observed for dehalogenations, acid gas sequestering, and other reactions (9, 10).

As a typical solid base, MgO has been shown to be active for butene isomerization at elevated temperatures (11). The major thrust of the work reported herein was to determine if superbase catalysts prepared from nanocrystalline MgO would be superior to those prepared from normal, fine MgO crystallites.

EXPERIMENTAL METHODS

1. *Preparation of MgO Samples: AP-MgO (nanocrystals prepared by an aerogel procedure) and CP-MgO (fine crystals prepared by a conventional procedure)*

The aerogel procedure to prepare AP-MgO has been described previously (9, 13), and consists of hydrolysis of $Mg(OCH_3)_2$ in a methanol–toluene mix. The resultant alcogel is dried under hypercritical conditions to form $Mg(OH)_2$ aerogel, which is dehydrated under vacuum at 500°C yielding AP-MgO of 350–500 m^2/g and 4.2 nm crystallites. Surface areas were measured by nitrogen gas adsorption (BET method).

Conventionally prepared (CP-MgO) samples were prepared by boiling commercially available MgO (Aldrich) for 5 h, drying at 120°C for 5 h, and then dehydration under vacuum at 500°C, yielding CP-MgO of 130–200 m^2/g with 8.8 nm crystallite size.

2. *Preparation of Super Base Catalysts*

The apparatus used was an inert atmosphere Schlenk tube bearing a side tube. The main tube was charged with 1.0 g MgO and the desired amount of freshly cut potassium was placed in the side tube. The system was evacuated and the side tube heated to about 300°C for 30 min. All of the potassium metal was evaporated and condensed/adsorbed by the MgO (held near room temperature), while the MgO was stirred magnetically. The potassium was very strongly adsorbed as evidenced by no visual changes during use, such as color change or deposits of potassium on other parts of the catalytic reactor.

---

[1] To whom correspondence should be addressed.

0021-9517/99 $30.00

3. *Isomerization of Alkenes*

2,3-Dimethyl-1-butene and 1-pentene (Aldrich) were dried over 4 Å molecular sieves at room temperature. Liquid alkene was injected onto the catalyst in the argon filled flask. The K/MgO catalyst and alkenes were stirred for 30 min at a desired temperature. Analyses were carried out on an OV-101 GC column at 120°C with helium flow of 30 ml/min.

4. *Alkylation of Alkenes*

A Hastaloy-C 250 ml autoclave was placed in an inert atmosphere box and loaded with 0.3 g of K/MgO catalyst. The autoclave was removed from the inert atmosphere box and evacuated. Propene gas was allowed to expand into the autoclave at a desired pressure, usually 100 psig. Then the propene was condensed by placing the autoclave in a dry-ice/acetone bath. Then ethylene gas was allowed to expand into the autoclave to a desired pressure. Moles of alkenes were calculated by PV relationships. The sealed autoclave was heated to a desired temperature for a specified time (usually 2 h) with stirring. After reaction, volatile products were collected in cold traps (−78° and −196°C) under vacuum. The conversion of reactants is defined as the total mass of products/mass of reactants. Analyses were carried out on a 30-m Rex-1 capillary column. The temperature was raised from room temperature up to 230°C at 10°C/min.

RESULTS AND DISCUSSION

1. *Isomerization of Alkenes*

It is well known that strong solid base catalysts can cause isomerization of alkenes through allylic carbanion intermediates. For example, Suzukamo and co-workers (4, 5) found Na/NaOH/Al_2O_3 to be active for isomerization of 2,3-dimethyl-1-butene at room temperature. Similarly,

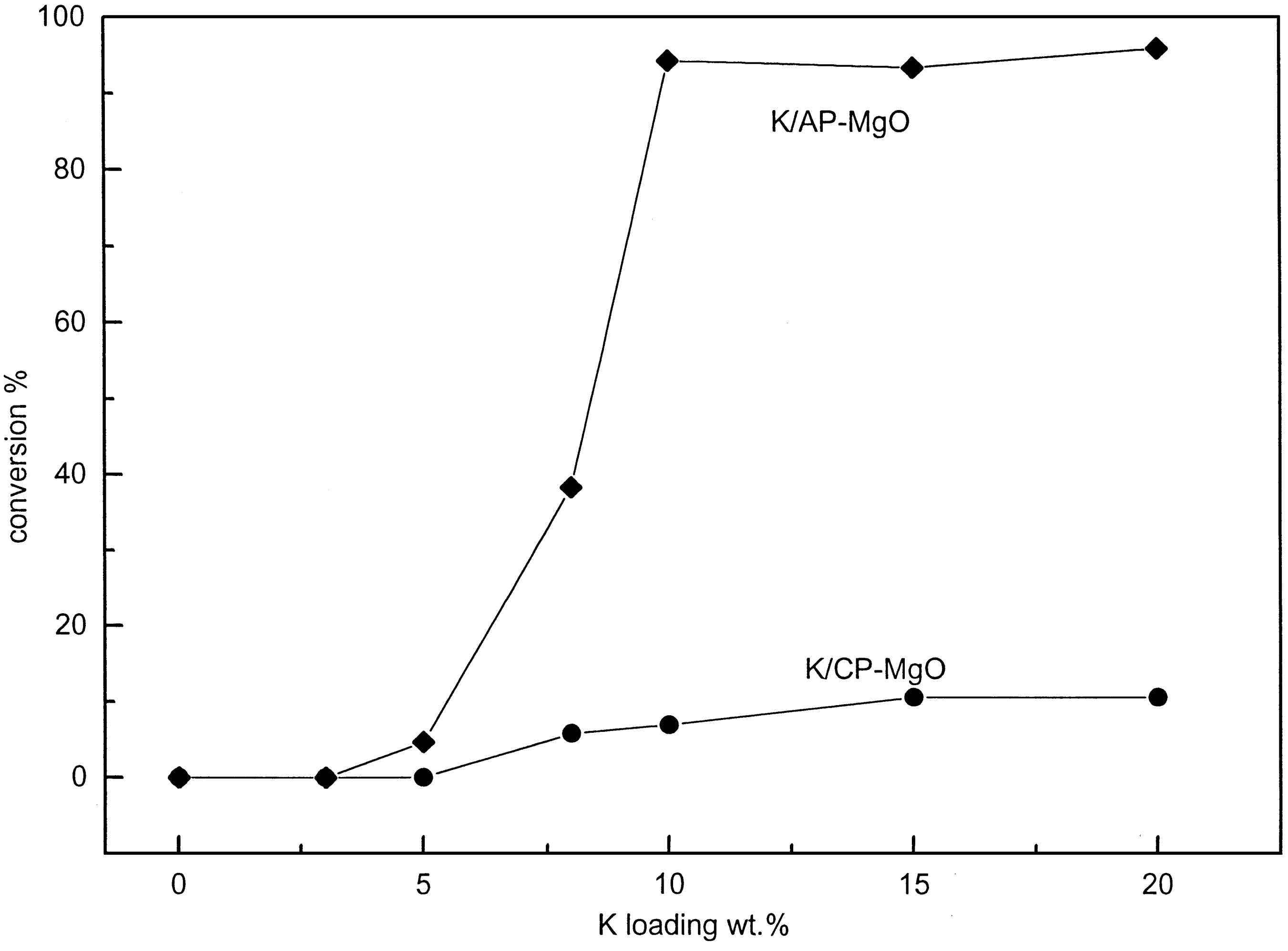

FIG. 1. Effect of K loading on the activity of K/AP-MgO and K/CP-MgO. 2 ml 2,3-dimethyl-1-butene, 0.1 g K/MgO, room temperature, 30 min. The % conversion refers to the percentage of starting material that was consumed.

Malinowski and co-workers also reported high activity of Na/MgO for isomerization (14).

We have been interested in determining if solid bases in nanocrystalline form behave differently compared with more conventional crystalline samples (8, 9, 12, 15). Therefore, we chose to investigate nanocrystalline MgO (AP-MgO for aerogel prepared), which has been well characterized in earlier studies (9, 13). This material has a surface area ranging from 350–500 m^2/g and the crystallites are polyhedral in shape exhibiting many crystal edges and corners (9).

For comparison, fine crystalline MgO (CP-MgO for conventionally prepared) was also studied, and this material has a surface area of 130–250 m^2/g and exists as hexagonal platelets or cubes, thus possessing a much lower ratio of edge–corner ions/total surface ions (9). Commercially available MgO (CM-MgO) possesses much lower surface area, about 30 m^2/g, and was found to be quite unreactive compared with either CP or especially AP samples.

These undoped samples were prepared and heat treated at 500°C under vacuum, cooled to room temperature, and then exposed to various alkenes, and no isomerization activity was found. Therefore, even nanocrystalline MgO does not possess base sites strong enough to catalytically remove allylic protons from 1-pentene or 2,3-dimethyl-1-butene. Both AP-MgO and CP-MgO were treated with potassium vapor, which adsorbed onto the powders. Loadings of K ranged from 1 to 20% by mass. Each sample (0.1 g) was then allowed to contact 2 ml of liquid 2,3-dimethyl-1-butene at room temperature for 30 min. Analysis by GC showed % conversion of starting material (Fig. 1) and the main product to be tetramethylethylene.

The activity of the nanocrystalline sample K/AP-MgO was much higher than the K/CP-MgO. In fact the differences are striking, with nearly 100% conversion for 10, 15, or 20% loadings of potassium for K/AP-MgO, but only about 10% conversions for similar loadings on K/CP-MgO. It is clear that surface area differences (128.3 m^2/g for K/AP-MgO and 83.4 m^2/g for K/CP-MgO; note that the potassium treatment lowered surface area from about 400 to 130 m^2/g for AP-MgO and from 150 to 83 m^2/g for CP-MgO) cannot explain such large reactivity differences.

Note that none of the samples were reactive when K loadings were 5% or lower. This is probably due to the sacrificial reaction of K metal with residual surface -OH groups ($2K + 2\text{-}OH \rightarrow 2\text{-}OK + H_2$). Indeed, it is known that

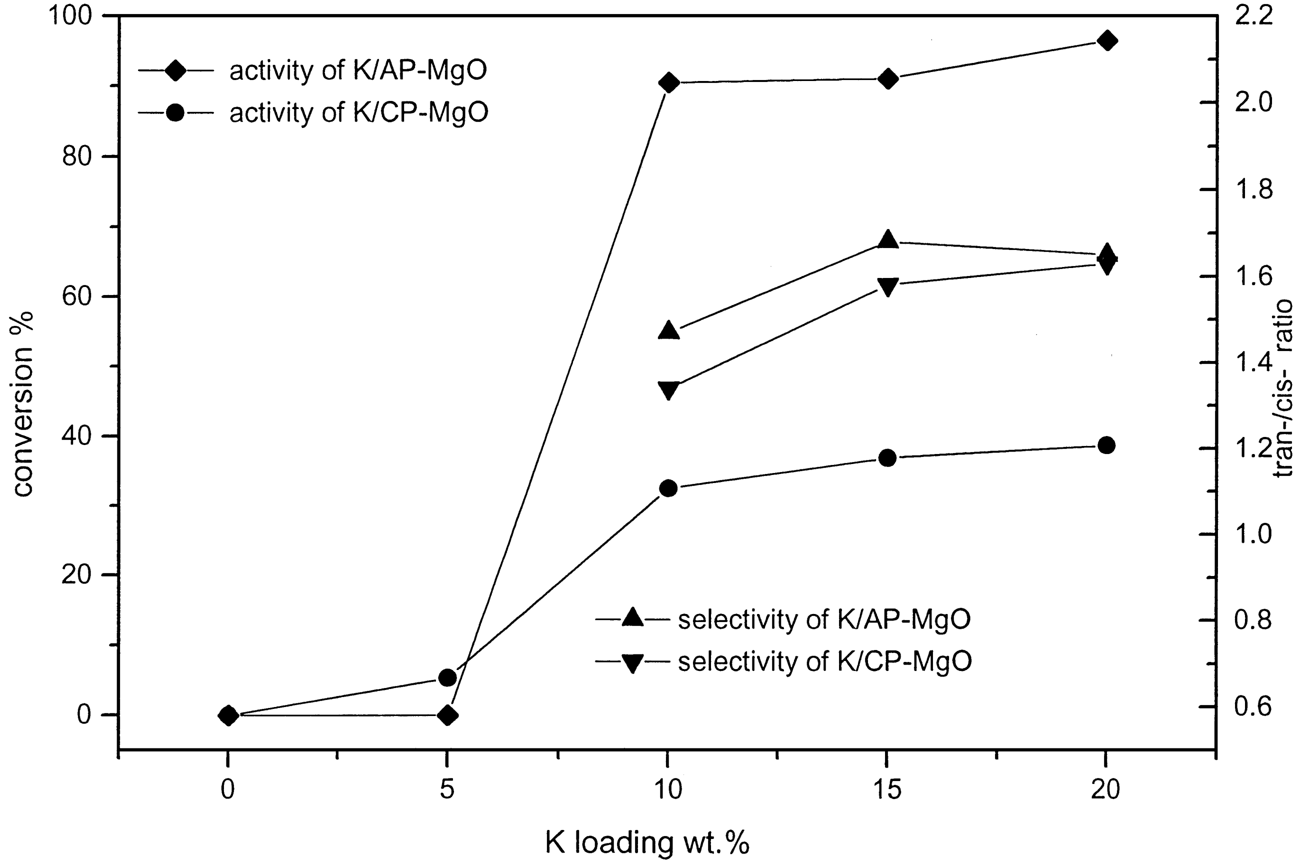

FIG. 2. Effect of K loading on the activity of 1-pentene isomerization. 3 ml 1-pentene, 0.1 g K/MgO, 0°C, 30 min. The % conversion refers to the percentage of starting material consumed, and trans/cis ratio refers to the 2-pentene products.

4–5 -OH groups/nm^2 exist on AP-MgO and CP-MgO after 500°C vacuum treatment (8, 9). This is approximately two surface -OH groups to one potassium atom, implying that conversion of about half the -OH group is sufficient for the onset of the formation of active superbase sites (16).

Similar results were observed for 1-pentene isomerization (Fig. 2). With low K loadings, no activity was evident, while at 10% loading the K/AP-MgO caused 90% conversion even at 0°C, again showing much higher activity than corresponding K/CP-MgO samples. On the other hand, selectivities to tran/cis-2-pentene were nearly the same for AP or CP samples.

2. *Alkylation of Toluene and Propylene by Ethylene*

At higher reaction temperatures, these catalysts are capable of alkylation reactions, although only certain types. Suzukamo and co-workers report that their $Na/NaOH/Al_2O_3$ was active for ethylene alkylation of cumene > ethylbenzene > toluene; e.g., $C_6H_5CH(CH_3)_2 + C_2H_4 \rightarrow C_6H_5C(CH_3)_2(C_2H_5)$ (4, 5). Moreover, K/Al_2O_3 has been found to be active for the cumene–ethylene reaction as well (17).

Interestingly, our catalysts were not active for cumene–ethylene alkylation, although the K/AP-MgO was active for toluene- ethylene alkylation and for toluene–propylene

$$C_6H_5CH_3 + H_2C{=}CH_2 \rightarrow C_6H_5CH_2CH_2CH_3$$

$$C_6H_5CH_3 + CH_3CH{=}CH_2 \rightarrow C_6H_5CH_2{-}CH(CH_3)_2$$

The most striking results were obtained when propylene–ethylene mixtures were studied. At a molar ratio of 1 : 1 propylene–ethylene alkylation

$$CH_3CH{=}CH_2 + H_2C{=}CH_2 \rightarrow \text{pentenes} + \text{heptenes}$$

took place as low as 140°C, with maximum conversions at 210°C for K/AP-MgO, and that activity decreased upon going to 240°C (18). There are two interesting points:

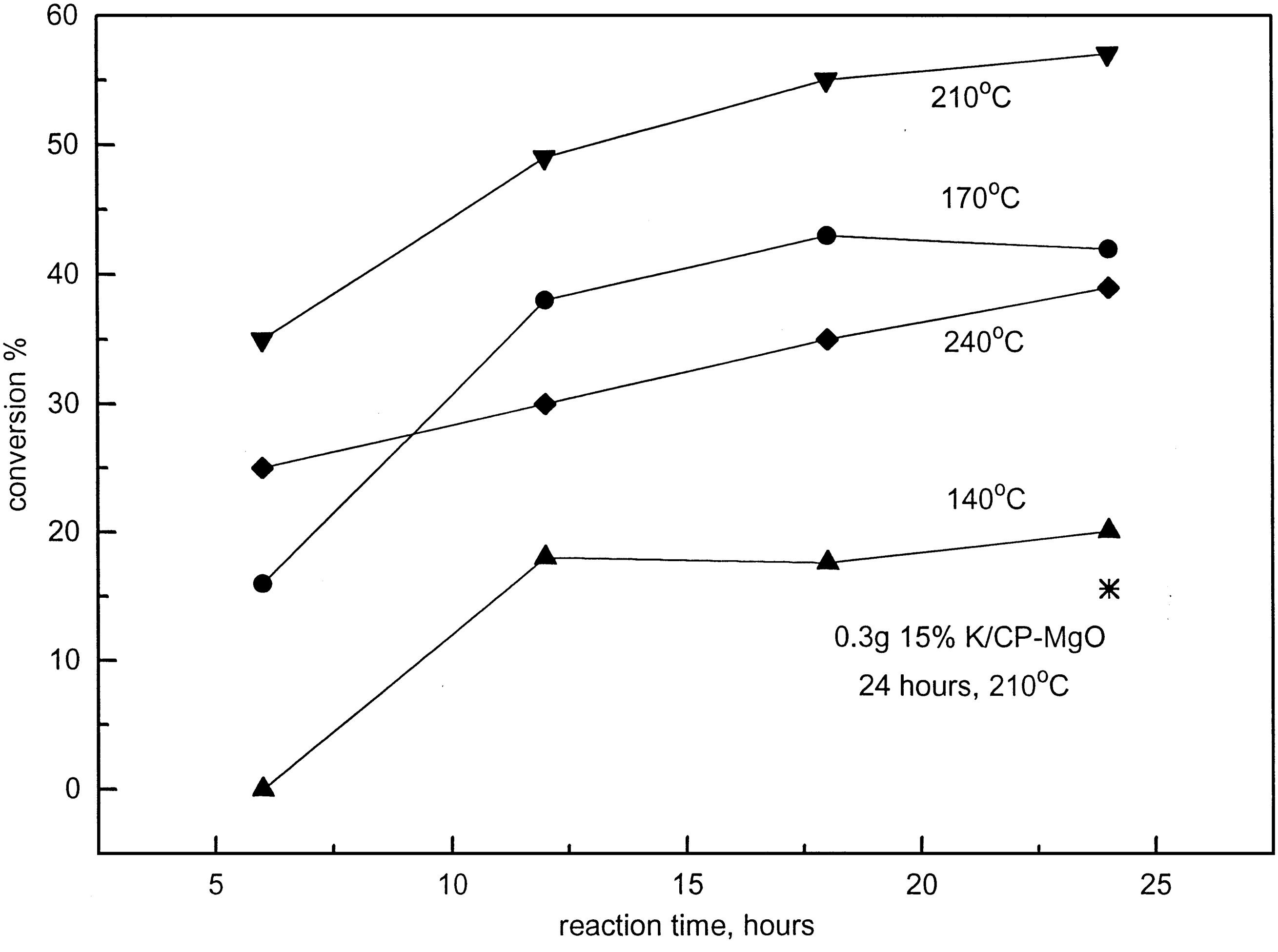

FIG. 3. Alkylation of ethylene and propylene. 0.3 g K/MgO, 100 psig ethylene, 100 psig propylene. The % conversion refers to the total mass of products/mass of reactants.

(a) again the AP sample was much more active than the CP samples, and (b) that above 210°C the catalytic reaction is suppressed (see Figs. 3 and 4). We believe this may be due to loss of potassium dispersion, perhaps by causing loss of strongly basic sites due to K sintering.

3. *Base Site Characterization of Samples*

The base strength of a solid can be defined as its proton–accepting ability and is quantified by the Hammett–Deyrup H-function (19). It is assumed that if a solid base can change the color of an indicator, the base strength of the solid is greater than or at least equal to the pK_{BH} of the indicator.

Several indicators have been used to determine base strength and base strength distributions, and we have employed 2,4-dinitroaniline ($pK_{BH} = 15$), 4-chloro-2-nitroaniline ($pK_{BH} = 17.2$), aniline ($pK_{BH} = 27$) and toluene ($pK_{BH} = 35$) and employed the method of Take and coworkers (20).

TABLE 1

The Basic Strength Distribution of Different Samples[a]

pK_{BH}	15 to 17.2	17.2 to 27	27 to 35	>35	Total meq/g
CP-MgO	0	0.35	0	0	0.35
AP-MgO	0.2	0.4	0.2	0	0.8
10% K/AP-MgO	0	0.9	0.5	0.15	1.55
15% K/AP-MgO	0	0.95	0.45	0.2	1.6
10% K/CP-MgO	0.1	0.6	0.1	0	0.8

[a] The pK_{BH} ranges and the method used are taken from Take and coworkers (20) and is an indicator–color change procedure done in hexane solvent.

In Table 1 the data are collected and show that AP-MgO possesses more and stronger basic sites than CP-MgO. Since AP-MgO exists as polyhedral-shaped nanocrystals with a higher ratio of edge/corner ions to total surface ions than CP-MgO (9), these data could be rationalized by the argument that low coordination O^{2-} ions on edges and corners

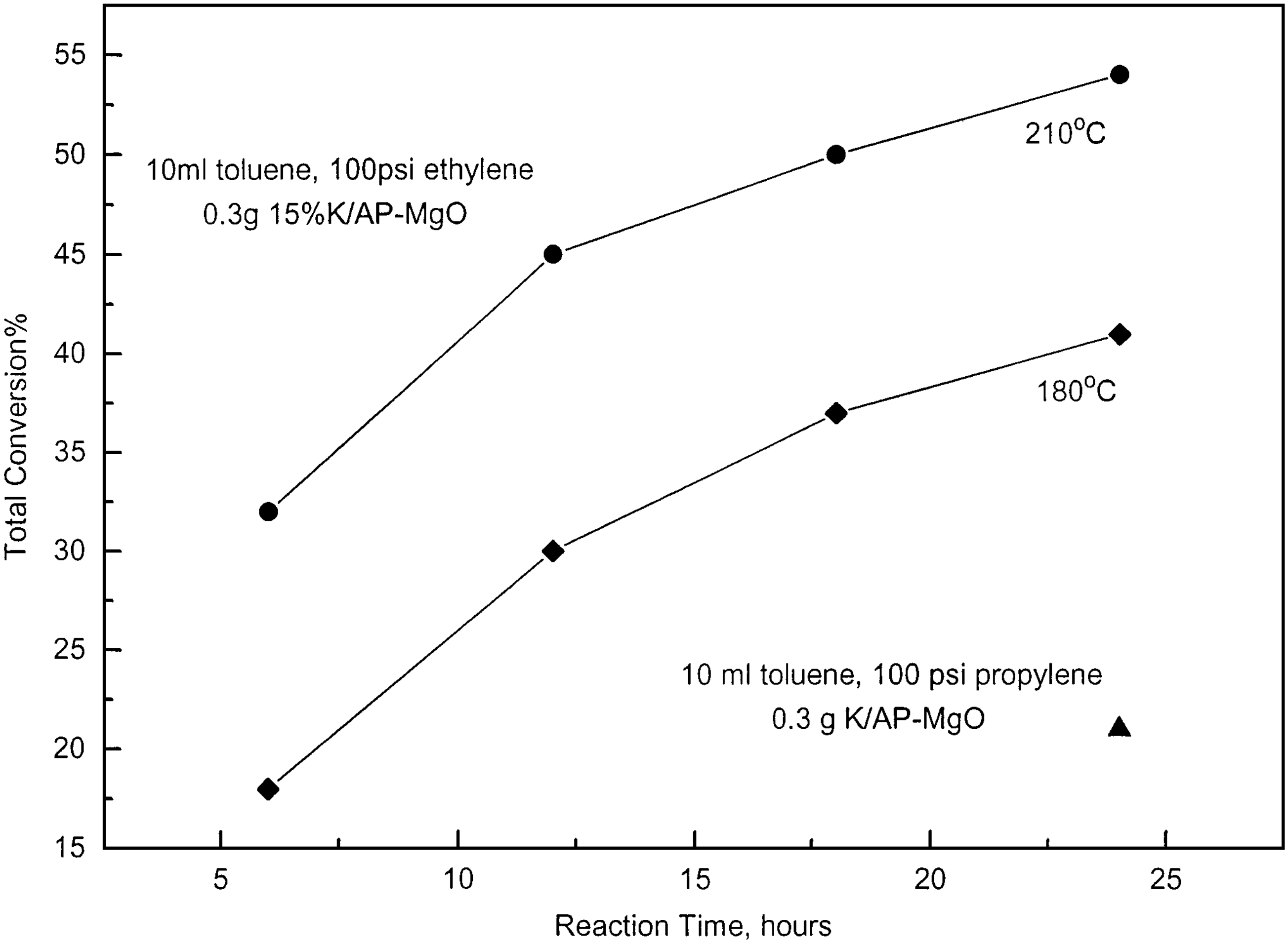

FIG. 4. Alkylation of toluene and ethylene. Total conversion refers to the weight percentage of liquid products over weight of starting materials.

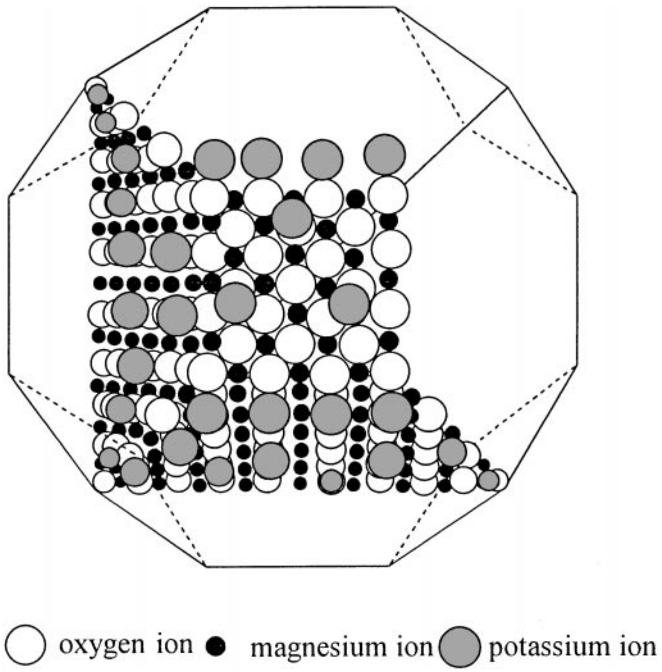

FIG. 5. Schematic structure of K/AP-MgO. K^+ are located at the edge/corner and adjacent sites. All particles are drawn to scale.

are less stabilized by adjacent Mg^{2+} ions (fewer of them) (1) and so could exhibit higher basicities. Actually, earlier calculations predict that about 20% of surface ions on AP-MgO are on corners or edges (9). Since 4-nm crystallites are approximately 30% surface, then 0.2×0.3 would suggest that 6% of all the ions are on edges or corners, and this corresponds to 1.5 mmol MgO on edges–corners/g MgO. This value of 1.5 mmol/g is reasonably close to the 0.8 mmol/g total base sites observed experimentally (Table 1).

Nevertheless, these base sites are in the range of 15–35 (not above 35) and are not strong enough to catalyze alkene isomerization or alkylation reactions, as discussed previously. Upon potassium doping, surface base site concentrations increase and, most importantly, stronger sites are generated, and these are likely to be the active sites in the isomerization and alkylation reactions observed, since AP-MgO and CP-MgO are not active in the absence of potassium. Also, it should be noted that the surface concentration of strongly basic sites correlates with the observed catalytic activities; that is, K/AP-MgO > K/CP-MgO.

Comparing the 10 and 15% potassium loadings, there is only a very slight increase in total base sites generated, and it is rather startling that the total base sites agree almost exactly with the calculated edge/corner sites predicted or 1.5 to 1.6 mmol/g of AP-MgO. It would appear that the structural nature of the active sites clearly has a great deal to do with low coordination ions (edges/corners) available on the surface.

Based on a recent ESR study of paramagnetic sites generated by Na doping of MgO (21), it is apparent that the Na^+ e^- pair does not have to be local. In other words, trapped electrons *near* edge/corner sites could cause enhancements in basicity at the edge/corner sites. Perhaps such a model is the best working hypothesis for the evidence that highly basic sites are generated by Na or K doping, and the number of total base sites correlates with the estimated number of corner/edge sites available. A drawing of such a transformation is shown in Fig. 5 (23).

CONCLUSIONS

Nanocrystalline MgO doped with potassium metal possesses basic sites capable of alkene isomerization and dimerization, including propylene–ethylene conversion to pentenes and hexenes. The activities of the AP samples exceed those of the CP samples, and greatly exceed those of CM-MgO. Furthermore, the active sites available correspond closely with the expected surface concentration of edge/corner sites on a polyhedral nanocrystal of MgO. Turnover number can be estimated based on the conversion per unit time and the strongly basic sites available. For example, 0.1 g 10% loaded K/AP-MgO sample possesses 0.015 mmol strongly basic sites ($H \geq 35$), and converts 0.016 moles of 2,3-dimethyl-1-butene to tetramethylethylene in 1800 s, yielding a TON of 0.59 s^{-1} for 10% K/AP-MgO (22).

ACKNOWLEDGMENT

The support of the Army Research Office is acknowledged with gratitude.

REFERENCES

1. Tanabe, K., Misono, M., Ono, Y., and Hattori, H., *in* "New Solid Acids and Bases," pp. 38, 212. Elsevier, Amsterdam, 1989.
2. Matsuhashi, H., and Arata, K., *J. Phys. Chem.* **99**, 11178 (1995).
3. Haag, W. O., and Pines, H., *J. Am. Chem. Soc.* **82**, 387 (1960).
4. Suzukamo, G., Fukao, M., and Minobe, M., *Chem. Lett.* **3**, 585 (1987).
5. Suzukamo, G., Fukao, M., Hibi, T., Tanaka, K., and Chikaishi, K., *in* "Acid-Base Catalysis" (K. Tanabe, H. Hattori, T. Yamaguchi, and T. Tanaks, Eds.), Proc. Int. Symp. Acid-Base Catalysis, p. 405. VCH, Basel, 1989.
6. Gesser, H. D., and Goswami, P. C., *Chem. Rev.* **89**, 765 (1989).
7. Fendler, J. H., *Chem. Rev.* **87**, 877 (1987).
8. Itoh, H., Utamapanya, S., Stark, J. V., Klabunde, K. J., and Schlup, K. J., *Chem. Mater.* **5**, 71 (1993).
9. Klabunde, K. J., Stark, J., Koper, O., Mohs, C., Park, D. G., Decker, S., Jiang, Y., Lagadic, I., and Zhang, D., *J. Phys. Chem.* **100**, 12142 (1996).
10. Schneider, M., and Baiker, A., *Catal. Rev.-Sci. Eng.* **37**(4), 515 (1995).
11. Matsuda, T., Tanabe, J., Hayashi, N., Sasaki, Y., Miura, H., and Sugiyama, K., *Bull. Chem. Soc. Jpn.* **55**, 990 (1982).
12. (a) Stark, J., Park, D. G., Lagadic, I., and Klabunde, K. J., *Chem. Mater.* **8**, 1904 (1996); (b) Stark, J., and Klabunde, K. J., *Chem. Mater.* **8**, 1913 (1996).
13. Utamapanya, S., Klabunde, K. J., and Schlup, J. R., *Chem. Mater.* **3**, 175 (1991).
14. Kijenski, J., and Malinowski, S., *React. Kinet. Catal. Lett.* **3**, 343 (1975).

15. Koper, O. B., Lagadic, I., and Klabunde, K. J., *Chem. Mater.* **9**, 838 (1997).
16. There are about 400 m^2/g AP-MgO or 400×10^{18} nm^2. If each nm^2 contains 5 surface -OH groups, then there would be 2×10^{21} surface-OH available. If a 5% loading of K were used, this would be 0.05 g, or about 7.7×10^{20} atoms of potassium, approximately 2 potassium atoms/nm^2.
17. Baba, T., Handa, H., and Ono, Y., *J. Chem. Soc. Faraday Trans.* **90**, 187(1994).
18. Pines, Herman., *in* "The Chemistry of Catalytic Hydrocarbon Conversions," p. 135. Academic Press, New York, 1981.
19. Hammett, L. P., *in* "Physical Organic Chemistry," p. 269. McGraw-Hill, New York, 1940.
20. Take, J., Kikuchi, N., and Yoneda, Y., *J. Catal.* **21**, 164 (1971).
21. Matsuhashi, H., and Klabunde, K. J., *Langmuir* **13**, 2600 (1997).
22. The catalysts were in powder form; 10% K/AP–MgO possesses a pore volume of 0.64 cc/g and average pore diameter of 121 Å, while 10% K/CP–MgO has pore volume 0.58 cc/g and average pore diameter 192 Å. These pores are believed to be the spaces between weakly packed nano- or microcrystals. Those pore sizes are much greater than the sizes of the small molecules we investigated. Also, the low activity K/CP–MgO samples actually have greater pore sizes than high activity K/AP–MgO. So, we believe the activity difference between K/AP–MgO and K/CP–MgO was not caused by mass stransfer limitations.
23. Calculation of K atoms:

$$\begin{aligned}\text{10\% K/AP-MgO, 0.1 g K} &= 2.56 \times 10^{-3}\ \text{mole}\\ &= 1.54 \times 10^{21}\ \text{K atoms}\\ &= 370\ \text{K atoms/particle}\end{aligned}$$

There are 270 edge/corner O atoms in each particle, so there are 1.4 potassium atoms on each edge/corner O^{2-}.