JOURNAL OF CATALYSIS **125**, 421–426 (1990)

# Different Activities and Selectivities of Silica–Alumina Catalysts Synthesized in Aqueous and Alcohol Solvents

P. YARLAGADDA, C. R. F. LUND, AND E. RUCKENSTEIN[1]

*Department of Chemical Engineering, State University of New York at Buffalo, Amherst, New York 14260*

Received January 30, 1990; revised April 16, 1990

Silica–aluminas having 15 wt% $Al_2O_3$ and subjected to identical heat treatment were synthesized starting from (i) sodium silicate and aluminum nitrate in water (ASA) and (ii) tetraethyl orthosilicate and aluminum isopropoxide in ethanol solvent (SA-SG). Both catalysts possess strong Brønsted acid sites which are capable of oligomerizing propene or ethene. With methanol as a feed, only ASA had a high hydrocarbon yield, while SA-SG produced mostly the dehydration product, dimethyl ether. While SA-SG possesses strong acidic sites, it is suggested that these sites become ineffective because of the strong chemisorption of the water resulting from dehydration. The weaker acidic sites also present on the SA-SG catalyst are probably responsible for the formation of the dehydration product.

## INTRODUCTION

Numerous investigations (*1–5*) on amorphous aluminosilicates have shown that their activity in acid-catalyzed reactions depends to a great extent on the amount of alumina present in the catalyst and to a lesser extent on other factors such as the method of preparation and the temperature at which the samples were heat treated prior to reaction. The nature of the acid sites present on the amorphous silica–aluminas, whether of Brønsted or Lewis type or both, has been the subject of innumerable studies (*6–9*), but still there is no consensus regarding the origin of these sites. However, it is widely accepted that the generation of these acid centers is due to the isomorphous substitution of $Si^{4+}$ by $Al^{3+}$ in the silica lattice (*10–12*) which generates an exchangeable cation. This aluminum ion can coordinate to oxygen either tetrahedrally or octahedrally or a combination of both. The relative amounts of these coordination states depend both on the alumina content in the sample and on the temperature at which it was heat treated. It has been shown (Table 1 of Ref. *13*) that the $Al^{IV}/(Al^{IV} + Al^{VI})$ ratio is independent of the alumina content when it is less than ca. 30 wt%; above this amount, the fraction of $Al^{IV}$ decreases. It has also been observed that when silica–alumina is heated at 700°C for 24 h, all aluminum present in the sample becomes located in tetrahedrally coordinated sites, over the entire range of alumina content.

The activity of the aluminosilicates in acid-catalyzed reactions depends on the total amount of Brønsted and Lewis acid sites, as well as on the acid strength distribution. Two types of Brønsted acid sites are known: (i) bridged hydroxyl groups and (ii) water molecules coordinated to a trigonal aluminum atom (the trigonal aluminum itself being a Lewis acid site). Recent studies (*14*) have shown that the hydroxyl groups of the amorphous aluminosilicates are quite similar in their acidic and spectral features to those present in zeolites, but their concentration is much lower. Since only the tetrahedrally held aluminum leads to the formation of a bridged hydroxyl group, it is obvious that the above sites are responsible for the catalytic activity. Thus, one can gen-

---

[1] To whom correspondence should be addressed.

0021-9517/90 $3.00

erally conclude that the $Al_2O_3/(SiO_2 + Al_2O_3)$ ratio and the conditions of heat treatment determine the tetrahedral versus octahedral aluminum sites and hence the catalytic activity. Recently we observed significant differences in the catalytic behavior of two types of silica–aluminas with a similar alumina content but synthesized from gels formed in water and ethanol solvents, and the results are presented herein.

## EXPERIMENTAL

Silica–alumina samples were prepared by cogelation starting with different sources of silica and alumina and in an aqueous or ethanol medium.

(*i*). *Silica–alumina synthesized in an aqueous medium (ASA).* To a 500-ml batch of 0.15 *M* aqueous sodium silicate (Fisher Scientific) solution whose pH was initially adjusted to 4 by the addition of 0.2 *M* hydrochloric acid, 250 ml of 0.06 *M* aqueous aluminum nitrate (Baker) was added. The pH of the above mixture was adjusted to about 6.5 by dropwise addition of 0.2 *M* $NH_4OH$ solution under vigorous stirring. The resulting gel was allowed to age for 24 h at room temperature under slow stirring and then was filtered. The resultant cake was thoroughly washed with distilled water, dried at 100°C overnight, and calcined at 600°C for 1 h in air. Later, the sample was treated with 1 *M* aqueous $(NH_4)_2SO_4$ solution at room temperature for 3 h. Finally, this $NH_4^+$ exchanged sample was calcined at 550°C for 1 h. Chemical analysis carried out by Galbraith Laboratories showed that the above sample, designated as ASA, contained 15.5 wt% $Al_2O_3$, and 0.07 wt% Na. Before the ammonium exchange, the Na level was 0.82 wt%. The BET surface area ($N_2$ as adsorbent) and the pore volume were 410 $m^2\ g^{-1}$ and 0.69 $cm^3\ g^{-1}$, respectively. X-ray powder diffraction showed the sample to be amorphous.

(*ii*). *Silica–alumina synthesized in an ethanol-rich medium (SA-SG).* The pH of a solution containing 30 ml of tetraethyl orthosilicate (Aldrich) dissolved in 200 ml of ethanol was adjusted to pH $\leqq 1$ by adding nearly 8 ml of nitric acid. To the above solution, 5 g of powdered aluminum isopropoxide (Aldrich) was added, and the whole mixture was stirred until all the aluminum isopropoxide had dissolved. Subsequently, the pH of the solution was adjusted to nearly 8.5 by adding 20 ml of 14% aqueous ammonia solution, under stirring. At this stage, a thick gel formed, to which, in order to be able to filter, an additional amount of 200 ml ethanol was added and the whole mass was kept under agitation overnight at room temperature. The mixture was filtered and the cake was washed with ethanol. After the cake was dried overnight at 70°C in vacuum, the sample was subjected to $NH_4^+$ exchange and to heat treatment under the conditions described earlier. The sample, designated as SA-SG, was analyzed and found to contain 15 wt% $Al_2O_3$ and a sodium content less than 0.03 wt%. The BET surface of the sample was 490 $m^2\ g^{-1}$ and the XRD pattern showed it to be amorphous.

The infrared spectra of the silica–alumina samples were recorded with a Perkin–Elmer 727B instrument. A fine powder of the sample was thoroughly mixed with an equivalent amount of KBr (Baker) and the mixture was pressed under a pressure of 180 $kg\ cm^{-2}$ to obtain a thin plate. The pressed sample was heated at 400°C overnight in air and then transferred into a quartz cell with $CaF_2$ windows. Before the IR spectrum was recorded, the sample was further heated at 150°C inside the quartz cell and continuously purged with helium. The IR spectrum was recorded at room temperature with a grating placed in the path of the reference beam.

Temperature-programmed desorption (TPD) spectra of the silica–alumina samples were obtained using ammonia as the probe base molecule. Details of the TPD setup and the procedure adopted for recording the spectra are similar to those reported previously (*15*, *16*).

Methanol to hydrocarbon conversion and olefin (ethene and propene) oligomerization experiments were conducted in a fixed-bed microreactor, in the manner described elsewhere (*15, 17*). In order to clarify some mechanistic features, additional experiments were conducted with ethanol or isopropanol as feed. The silica–alumina samples, after having been loaded into the reactor, were maintained at the reaction temperature for 4 h in helium before the commencement of the reaction.

## RESULTS AND DISCUSSION

The activity and selectivity data obtained during the methanol conversion and olefin oligomerization reactions are given in Table 1. Silica–alumina catalysts deactivate rapidly (over ca. 10–20 h) and severely under methanol conversion conditions. The results in Table 1 were obtained after 2 h on stream, during which the catalysts deactivated by less than 5% of their fresh activity.

For the ethene or propene oligomerization reactions, both the ASA and the SA-SG catalysts led to comparable conversions. With regard to the selectivity, the following observations can be made: When ethene was the feed and SA-SG the catalyst, the selectivity was higher for the $C_3$, $C_4$ olefins; for the ASA catalyst, the selectivity was higher for the $C_4$ alkanes. More pronounced differences in selectivity were observed with propene as reactant; a larger fraction of $C_8$ and $C_9$ hydrocarbons were formed via polymerization, followed by cracking to aromatics, on the SA-SG catalyst.

A striking difference in the behavior of the two silica–alumina samples was, however, observed during the methanol conversion reaction. Table 1 shows that the conversion of methanol to hydrocarbons (excluding dimethyl ether) is around 94 mol% for the ASA catalyst and only 2.5% for the SA-SG catalyst, in spite of the fact that both catalysts have almost the same alumina content and have been heat treated in the same way. Furthermore, no hydrocarbons higher than $C_4$ were detected during the reaction over the SA-SG catalyst, while a wide spectrum of hydrocarbons has resulted over the ASA catalysts.

TABLE 1

Activity and Selectivity Data Obtained during Catalytic Reactions over the Silica–Alumina Samples

| | ASA | SA-SG |
|---|---|---|
| a. $CH_3OH$ conversion reaction (375 ± 5°C; 1.0 ± 0.1 $h^{-1}$ WHSV; 1 atm total pressure) | | |
| Conversion (mol%) | 94.2 | 2.5 |
| Selectivity (wt%) | | |
| $CH_4$ | 2.4 | 24.2 |
| Total $C_2$–$C_4$ olefins | 63.9 | 66.1 |
| Total $C_2$–$C_4$ alkanes | 17.1 | 9.7 |
| $C_{5+}$ nonaromatics | 11.6 | — |
| Aromatics | 5.0 | — |
| b. $C_3H_6$ oligomerization reaction (365 ± 5°C; 3.4 ± 0.1 $h^{-1}$ WHSV; 1 atm total pressure) | | |
| Conversion (mol%) | 8.4 | 8.1 |
| Selectivity (wt%) | | |
| $CH_4$ | 0.2 | 0.1 |
| $C_2H_4$ | 0.4 | 0.5 |
| $C_2H_6$ | 0.6 | 0.8 |
| $C_3H_8$ | 22.4 | 19.3 |
| $(i + n)\ C_4H_{10}$ | 4.7 | 6.2 |
| $C_4$ olefins | 51.6 | 48.1 |
| $C_5 + C_6$ | 5.2 | 2.9 |
| $C_7$ | 3.6 | 2.6 |
| $C_8$ | 6.1 | 10.3 |
| $C_9$ | 3.3 | 7.8 |
| $C_{9+}$ | 1.9 | 1.4 |
| | 100.0 | 100.0 |
| Total aromatics | 1.7 | 3.1 |
| c. $C_2H_4$ oligomerization reaction (410 ± 5°C; 3.7 ± 0.1 $h^{-1}$ WHSV; 1 atm total pressure) | | |
| Conversion (mol%) | 4.1 | 5.3 |
| Selectivity (wt%) | | |
| $CH_4$ | 0.1 | 0.2 |
| $C_2H_6$ | 9.2 | 8.0 |
| $C_3H_6$ | 15.0 | 20.9 |
| $C_3H_8$ | 5.4 | 2.5 |
| $(i + n)\ C_4H_{10}$ | 30.5 | 11.3 |
| $C_4$ olefins | 39.8 | 57.1 |

This difference might be attributed to the deactivation of the catalyst due to coking, but, as already noted, the activities of the catalysts after 2 h on stream (the only ones

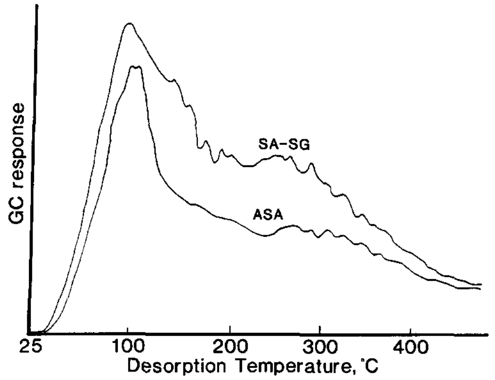

FIG. 1. Temperature-programmed desorption spectra of adsorbed ammonia for 0.23 g of SA-SG and 0.20 g of ASA.

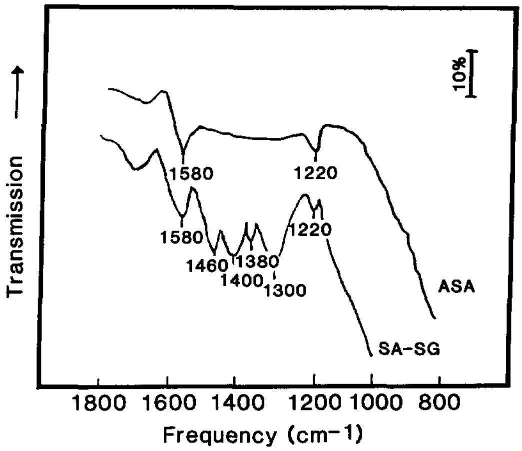

FIG. 2. IR spectra of silica–alumina samples.

listed in Table 1) had decreased by less than 5% of their initial activity. Therefore, the level of deactivation and/or coking does not appear to be responsible for the difference in behavior of the two catalysts.

Since the reactions occurring in the present study are acid catalyzed (*18–20*), it is likely that the difference in the behavior of the two catalysts can be related to their acidic characteristics. From the ammonia TPD spectra shown in Fig. 1, it is apparent that both the ASA and the SA-SG catalysts possess strong acid sites (sites from which ammonia desorbs above 200°C) which are heterogeneous in nature. The number of strong acid sites as well as the total number of acidic sites is greater on the SA-SG than on the ASA catalyst surface (using the spectral area as a measure of the acid sites after accounting for the sample weight).

Additional evidence for the presence of both strong and weak acid sites comes from the infrared spectra of the catalysts in the hydroxyl frequency range. The IR spectra of both catalysts in the frequency region of 1800–800 $cm^{-1}$ are shown in Fig. 2. Both samples exhibit absorption peaks at 1580 $cm^{-1}$, which can be ascribed to water molecules bound to octahedral aluminum ions (*21*). Such sites constitute weak acid sites. Interestingly, the SA-SG catalyst has additional peaks at 1460, 1400, 1380, and 1300 $cm^{-1}$ which are not present in the ASA catalyst. The absorption peak at 1460 $cm^{-1}$ is due to the water molecules coordinated either on an $Al^{IV}$–$Al^{VI}$ or an $Al^{VI}$–$Al^{VI}$ ion pair, which constitute relatively weak acid sites. The 1380 $cm^{-1}$ peak is due to the tetrahedrally coordinated aluminum ions (*21*) which lead to strong acid sites. The peaks at 1400 and 1300 $cm^{-1}$ have not yet been identified. However, it is known (*21*) that the peaks in the lower frequency region represent aluminum ions with coordination states smaller than 6 and, hence, with varying capabilities to coordinate water molecules leading to strong acidic sites.

Given the above TPD and IR features which indicate a greater number of strong acid sites for the SA-SG catalyst, the SA-SG catalyst would be expected to be more active than the ASA catalyst. However, experiment shows that: (1) SA-SG and ASA catalysts are oligomerizing ethene and propene in comparable conversions, and (2) the ASA catalyst produces higher hydrocarbons from methanol while the SA-SG catalyst produces only dimethyl ether. The fact that SA-SG catalyst produces only dimethyl ether and not higher hydrocarbons, may be due either to a geometrical arrangement of the sites such that they do not allow the initial C–C bond formation or, more likely, to their preference to chemisorb water molecules instead of organic moieties. Another possibility can be related to the difference in Na levels, since sodium is known to poison acid sites. However, it is the catalyst (ASA) with the greater amount of sodium (i.e., more sites poisoned) which is more active in the methanol conversion to hydrocarbons.

The methanol conversion process involves the formation of dimethyl ether by dehydration, primary C–C bond formation, and aromatization accompanied by hydrogen transfer (*22*). According to Parera and Figoli (*23*), the ether formation over amorphous silica–alumina involves a Brønsted acid site and occurs by the following steps:

$$CH_3OH + H^+ \rightarrow CH_3OH_2^+$$

$$CH_3OH_2^+ + CH_3OH \rightarrow (CH_3)_2O + H_2O + H^+$$

The formation of the initial C–C bond from dimethyl ether on the amorphous silica–alumina can be explained either by the rake mechanism (*25*) or by the alkoxonium route (*25*). In the former scheme, the chain growth occurs by carbene insertion into the surface alkoxy species, which are later transformed into olefins via a carbenium ion intermediate. The latter route involves the formation of a dimethyl oxonium ion by the interaction of the dimethyl ether with a Brønsted acid site which then reacts with another molecule of dimethyl ether to form trimethyl oxonium ion which, finally, via a Stevens-type intramolecular arrangement results in a methyl ethyl oxonium ion. Thus, the above mechanisms require at least one Brønsted acid site (alkoxonium) and preferably two adjacent acid sites in the rake mechanism for the C–C bond formation. In the case of SA-SG such sites or the necessary topological arrangement of such sites may be absent. Another possibility is that such sites, even if present, prefer to interact strongly with the water molecules released during the dehydration step. In support of the latter possibility is the fact that the IR spectrum in Fig. 2 of the SA-SG catalyst shows multiple peaks at frequencies below 1580 $cm^{-1}$; as already mentioned, these peaks are due to hydroxyl groups attached to Al cations of coordination less than 6, which are strong acid sites. Consequently, water and/or oxygenate molecules may bind strongly to these sites, thus partially poisoning the catalyst. The reactions which do proceed, such as the transformation of methanol to dimethyl ether, take place on the weak acid sites.

In order to confirm the difference in behavior of the two catalysts, we conducted experiments with other oxygenates (ethanol or isopropanol) as feed. Unlike methanol, upon dehydration both of these oxygenates lead directly to their corresponding olefins, namely, ethene and propene. (In contrast to methanol, the first C–C bond formation does not need in these cases two neighboring sites.) The resulting olefins could undergo further oligomerization reactions upon the acid sites. Interestingly, with the SA-SG catalyst, ethene formed from ethanol and propene from isopropanol with selectivities greater than 96 wt%. With both oxygenates only small amounts of other hydrocarbons were detected. In contrast, with the ASA catalyst, a wide range of hydrocarbon products were obtained from both ethanol and isopropanol. These results suggest that in the case of SA-SG, the acidic sites which are active in the oligomerization reactions are indeed easily poisoned with the water molecules formed during the dehydration reaction, the latter being strongly chemisorbed on these sites. The weaker acid sites which are also present on the SA-SG catalyst are responsible for the formation of the dehydration product.

Since the $SiO_2/Al_2O_3$ ratio and the heat treatment procedure are almost the same for both silica–aluminas, the environment during gel formation itself is likely to affect the generation of sites of specific coordination. In the case of zeolites, it has been shown (*26–28*) that the solvent in which the gel is formed plays an important role in determining the structure.

## CONCLUSIONS

The present work has shown that depending on the type of solvent in which the silica–alumina gels are prepared, the catalytic activity for oxygenate conversion to hydrocarbons can vary markedly while the activity for olefin oligomerization remains nearly constant. Thus, on the catalyst prepared in alcohol, the Brønsted acid sites responsible for oligomerization appear to be ineffective in the presence of water molecules released during the dehydration step. As a result, a low hydrocarbon yield is obtained. In contrast with the catalyst whose gel was prepared with water as a solvent, the hydrocarbon yield is large.

## ACKNOWLEDGMENTS

The experimental assistance of Mr. M. Schiek is highly appreciated. Occidental Chemical Corporation's financial support to C.L. through the NSF PYI program (CBT-8857100) is also appreciated and acknowledged.

## REFERENCES

1. Tanabe, K., "Solid Acids and Bases." Kodansha, Tokyo, 1970.
2. Tamele, M. W., *Discuss. Faraday Soc.* **8,** 270 (1950).
3. Ward, J. W., and Hansford, R. C., *J. Catal.* **13,** 154 (1969).
4. Mills, G. A., Boedecker, E. R., and Oblad, A. G., *J. Amer. Chem. Soc.* **72,** 1554 (1950).
5. Holm, V. C. F., Bailey, G. C., and Clark, A., *J. Phys. Chem.* **63,** 129 (1959).
6. Hirschler, A. E., *J. Catal.* **6,** 1 (1966).
7. Hansford, R. C., "Advances in Catalysis," Vol. 4, p. 17. Academic Press, San Diego, 1952.
8. Milliken, Jr., T. H., Mills, G. H., and Oblad, A. G., *Discuss. Faraday Soc.* **8,** 279 (1950).
9. Hall, W. K., Lutinski, F. E., and Gerberich, H. R., *J. Catal.* **3,** 512 (1964).
10. Thomas, C. L., *Ind. Eng. Chem.* **41,** 2564 (1949).
11. Leonard, A. J., Ratnasamy, P., Declerck, F. D., and Fripiat, J. J., *Discuss. Faraday Soc.* **52,** 98 (1971).
12. Miesserov, K. G., *J. Catal.* **13,** 169 (1969).
13. Leonard, A., Suzuki, S., Fripiat, J. J., and De-Kimpe, C., *J. Phys. Chem.* **68**(9), 2608 (1964).
14. Borovkov, V. Yu, Alexeev, A. A., and Kazansky, V. B., *J. Catal.* **80,** 462 (1983).
15. Yarlagadda, P., Lund, C. R. F., and Ruckenstein, E., *Appl. Catal.* **54,** 139 (1989).
16. Nelson, H., Lussier, R. J., and Still, M. E., *Appl. Catal.* **7,** 113 (1983).
17. Yarlagadda, P., Lund, C. R. F., and Ruckenstein, E., *Appl. Catal.,* in press.
18. Shephard, F. E., Rooney, J. J., and Kemball, C., *J. Catal.* **1,** 379 (1962).
19. Poutsma, M. L., *in* "Zeolite Chemistry and Catalysis" (J. A. Rabo, Ed.), ACS Monograph 171, p. 483. Amer. Chem. Soc. Washington, DC, 1976.
20. Chang, C. D., "Hydrocarbons From Methanol." Dekker, New York, 1983.
21. Vlaev, L., Damyanov, D., and Mohamed, M. M., *Colloids Surf.* **36,** 427 (1989).
22. Chang, C. D., and Silvestri, A. J., *J. Catal.* **47,** 249 (1977).
23. Parera, J. M., and Figoli, N. S., *J. Catal.* **14,** 303 (1969).
24. Cormerias, F. X., Perot, G., Chevalier, F., and Guisnet, M., *J. Chem. Res. Synop.* 362 (1980).
25. van den Berg, J. P., Wolthiuzen, J. P., and van Hooff, J. H. C., "Proceedings Fifth Conf. Zeolites, Naples, Italy, 1980," p. 649.
26. Bibby, D. M., and Dale, M. P., *Nature (London)* **317,** 157 (1985).
27. van Erp, W. A., Kouwenhoven, H. W., and Nanne, J. M., *Zeolites* **7,** 286 (1987).
28. Sand, L. B., "Molecular Sieves" (R. M. Barrier, Ed.), p. 71. Soc. Chem. Ind., London, 1968.