Journal of Catalysis **186**, 478–480 (1999)
Article ID jcat.1999.2560, available online at http://www.idealibrary.com on IDEAL®

RESEARCH NOTE

Concentration of Hydroxyl Groups on Silica Monolayer Solid Acid Catalyst

Naonobu Katada,[1] Toshiyuki Fujii, Koji Iwata, Yasushi Hibino, and Miki Niwa

Department of Materials Science, Faculty of Engineering, Tottori University, 4-101 Koyama-cho Minami, Tottori 680-8552, Japan

Received February 19, 1999

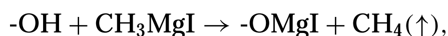
Adding silica to alumina has been known to generate the solid acidity (1) and thermal stability (2, 3). Although silica–alumina has been used for various catalytic reactions, most widely among solid acid catalysts, generation of these functions is difficult to understand, because the structure of the interface between alumina and silica, which often forms an amorphous phase, is complicated and hardly analyzed.

In order to obtain a model compound for the binary oxide catalyst containing silica, we have applied chemical vapor deposition (CVD) of silicon alkoxide to prepare a silica layer on alumina (4). The acidic property and thermal stability (5) were observed on the formed silica monolayer. It was clarified that the silica monolayer had a two-dimensional network of siloxane (6) mainly consisting of $Si(OAl)_1(OSi)_3$ species (7), and the monolayer protected the alumina particle from sintering like an eggshell at such a high temperature as 1493 K (5).

The origin of the thermal stability of the monolayer is speculated to be the stable Si–O–Al bond, which also makes for the ready formation of an ultrathin layer (8). On the other hand, the proposed structural model mainly consisting of $Si(OAl)_1(OSi)_3$ species suggests that the surface concentration of hydroxyl groups on the silica monolayer is low, and this is possibly another origin of the thermal and hydrothermal stability. In the present study we measured the hydroxyl concentration on the silica monolayer to confirm the structural model and to clarify the origin of thermal stability.

According to our previous paper (8), tetramethoxysilane [$Si(OCH_3)_4$] was deposited at 593 K on γ-alumina (JRC-ALO4 supplied by Catalysis Society of Japan as a reference catalyst, 161 $m^2\ g^{-1}$), which had been evacuated at 673 K, followed by final calcination at 673 K in oxygen. The amount of deposited silica was determined by monitoring the weight gain and is shown in the unit of Si-atom nm^{-2} by dividing by the BET surface area, which was measured with nitrogen adsorption at 77 K.

The measurements of hydroxyl groups using CH_3MgI were carried out principally according to the literature (9). The sample powder (0.5 g) was evacuated in a quartz cell at 673 K for 1 h. Then a solution of $CH_3MgI/C_2H_5OC_2H_5$ (ca. 2 mol dm^{-3}), which had been purified by distillation in the vacuum system, was added by rotating the cell. It was observed that the pressure in the system quickly increased from the vapor pressure of solvent up to a stable value. The increase of the pressure should show the pressure of the methane produced by the reaction



$$\text{-OH} + CH_3MgI \rightarrow \text{-OMgI} + CH_4(\uparrow),$$

and therefore the amount of hydroxyl groups was calculated from the amount of produced methane based on the pressure. The surface concentration of hydroxyl groups was determined by dividing the hydroxyl amount by the BET surface area.

Figure 1 shows the relationship between the OH concentration measured and Si concentration. The OH concentration on alumina evacuated at 673 K was ca. 7 nm^{-2}. In order to confirm the validity, the measurements on alumina were carried out with varied the sample amounts from 0.1 to 1 g. An almost constant value, 6.5 to 7.2 OH nm^{-2}, was observed, supporting the validity of the experiments. Moreover, the determined concentration was approximately in agreement with the previously reported values (5.5–6.5 OH nm^{-2}), as reviewed by Peri (10) and Knözinger and Ratnasamy (11).

The OH concentration gradually decreased with increase of the silica from 0 to 10 Si nm^{-2}, and it suddenly dropped at 13 Si nm^{-2}. The minimum concentration ca. 1.5 nm^{-2} was obtained. Subsequently, the decreased concentration again increased with 13–15 Si nm^{-2}, and again decreased at ca. 26 Si nm^{-2}.

At the beginning of the deposition, namely, at 0 to 10 Si nm^{-2} of the silicon concentration, the hydroxyl concentration was gradually decreased. This suggests that the silica covered the AlOH group, but a fraction of them were converted into SiOH. It is speculated that because the

[1] Corresponding author. Fax: +81-857-31-5684. E-mail: katada@chem.tottori-u.ac.jp.

0021-9517/99 $30.00
Copyright © 1999 by Academic Press
All rights of reproduction in any form reserved.

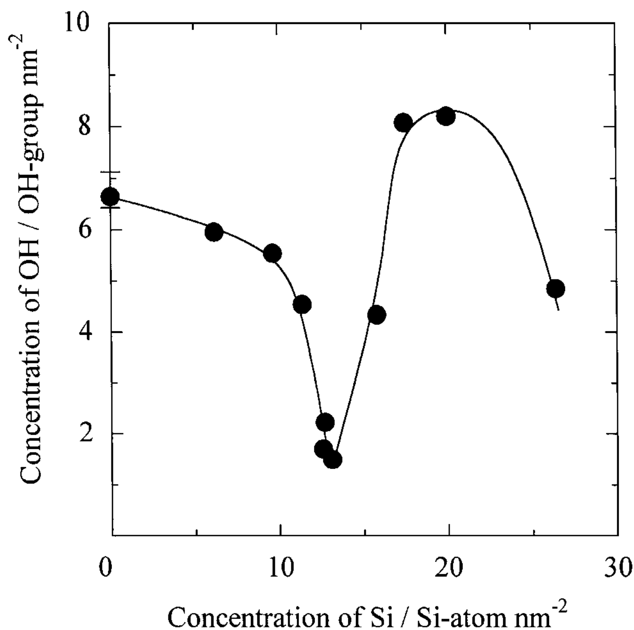


FIG. 1. Concentration of hydroxyl groups measured after evacuation at 673 K against concentration of deposited silica.

coverage was incomplete in this region, the SiOH locates on the edge of the silica layer, as shown in Scheme 1 (b).

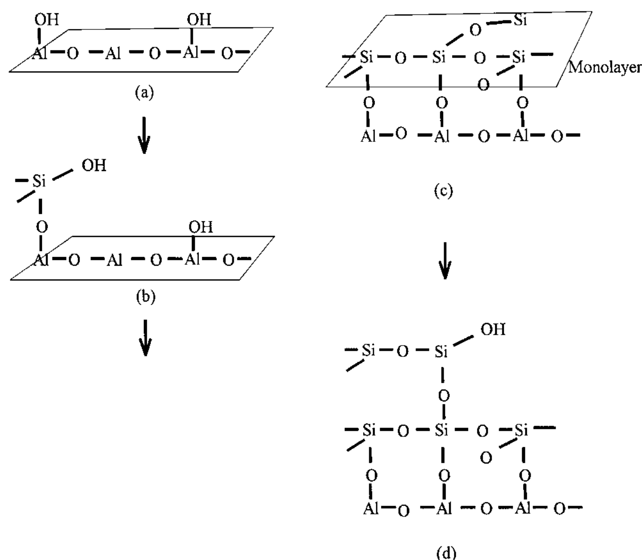
The silica monolayer covers the surface completely with 13 Si nm^{-2}, where the numbers of silicon and surface aluminum atoms are the same, as evidenced by the BAT experiments (4). At the same time, the present experiments showed the quite low concentration of OH, indicating that the silica monolayer has a quite low concentration of OH groups. As shown in Scheme 1 (c), it is suspected that the complete coverage with the silica layer almost completely diminished the hydroxyl groups.

We have proposed the structure of the silica monolayer consisting of the two-dimensional siloxane network (Scheme 1, c) on the basis of the stoichiometry of chemical vapor deposition (6). In this structure, the deposited silica mainly forms $Si(OAl)_1(OSi)_3$ species. In a fact, ^{29}Si NMR showed that the major species on the silica monolayer was $Si(OAl)_1(OSi)_3$, whereas a relatively small amount of $Si(OAl)_1(OSi)_2(OH)_1$ species was observed (7). The present low surface concentration of hydroxyl groups is in good agreement with these observations. A highly developed network structure of Si–O–Si is thus confirmed.

Further accumulation of silica again increased the hydroxyl content. As shown in Scheme 1 (d), SiOH can be formed on the edge of the accumulated layer. The second drop of hydroxyl concentration at 26 Si nm^{-2}, which corresponds to the double accumulation of silica layer, possibly shows the coverage by the double layer of silica.

The thermal stability of the silica monolayer has been reported (5). Alumina almost completely lost its surface area at 1493 K, but the silica-covered samples showed high surface areas. They showed a maximum about 60 $m^2\ g^{-1}$ with ca. 15 wt% of silica, which approximately corresponds to the monolayer, and decreased again with further accumulation of silica layer. From 5 to 15 wt% of the loading, it was observed that only the surface covered by silica was maintained but alumina-exposed surface was lost. After the high temperature calcination, the silica monolayer protected the particle from sintering like an eggshell (5).

In the present study, we measured also the hydrothermal stability of silica monolayer. As shown in Fig. 2, both



SCHEME 1. Models of alumina surface (0 Si nm^{-2}, a), submonolayer (6 Si nm^{-2}, b), monolayer (13 Si nm^{-2}, c) and doubly accumulated layer of silica (20 Si nm^{-2}, d).

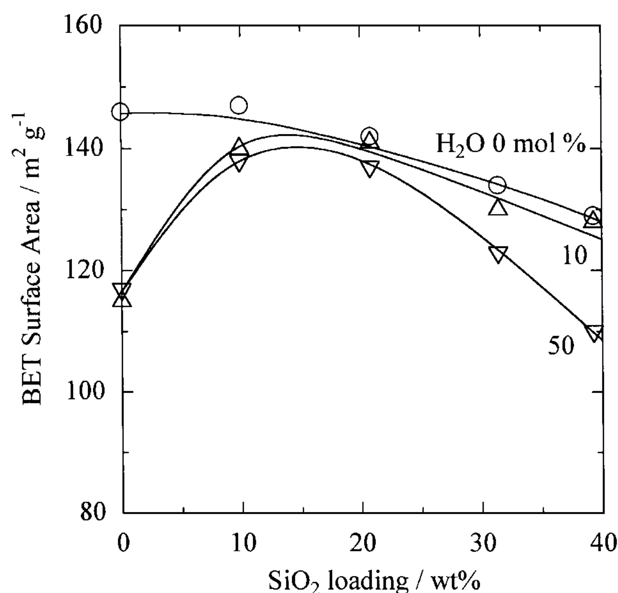


FIG. 2. BET surface area after treatment at 1073 K for 24 h in flowing helium with 0 (○), 10 (△), and 50 mol% (▽) water vapor.

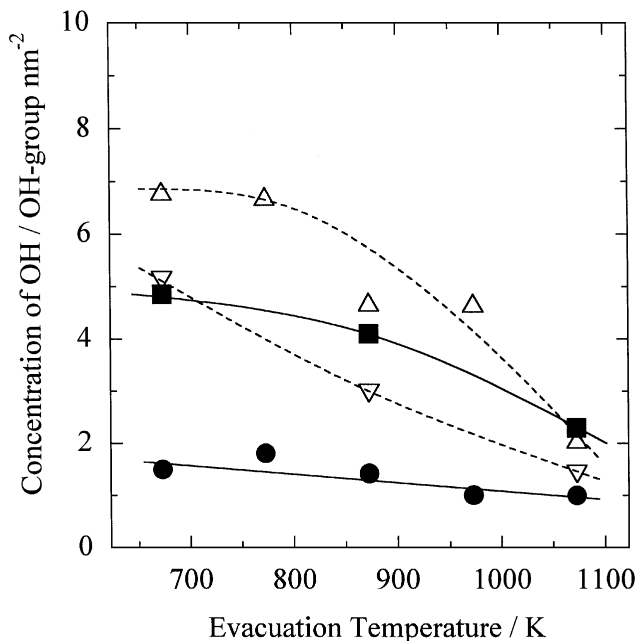


FIG. 3. Concentration of hydroxyl groups measured after evacuation at various temperatures on alumina (△), silica gel (▽), silica monolayer on (13.1 Si nm^{-2}, ●), and further accumulated silica layer on alumina (26.4 Si nm^{-2}, ■).

alumina and silica-coated samples did not lose surface area at this temperature (1073 K) unless water vapor was introduced. By adding 10 mol% water vapor the surface area of alumina was decreased to ca. 120 m^2 g^{-1}, while the silica-coated samples maintained their surface area. With 50 mol% water vapor, the sample with doubly accumulated layer (>30 wt% of the SiO_2 loading) also lost surface area, and the hydrothermal stability of the sample covered by the monolayer (20 wt%) was demonstrated.

Alumina, silica, and accumulated silica layer (20 Si nm^{-2}) possessed higher hydroxyl concentrations after evacuation at 673 K, and the concentration gradually decreased with increasing temperature, as shown in Fig. 3. This points out that the surfaces of these materials after the removal of hydroxyl groups, i.e., dehydration, have high capacity for rehydration. It is possible that the cycle of rehydration and dehydration repeatedly proceeds on these materials in a humid atmosphere. The dehydration of the surface,

$$2\text{M-OH} \rightarrow \text{M-O-M} + H_2O(\uparrow),$$

at a high temperature probably accompanies the formation of a grain boundary between two particles. This is considered to cause the hydrothermal sintering.

On the contrary, as naturally imaged from its low hydroxyl concentration at 673 K, almost constant hydroxyl concentration was observed on the silica monolayer with evacuation at 673 to 1073 K, as shown in Fig. 3. The constant concentration of hydroxyl groups is suggested to be one origin of the thermal stability generated by the silica monolayer.

ACKNOWLEDGMENT

This study was partly supported by a Grant-in-Aid from the Ministry of Education, Science, Sports and Culture, Japan (10555278).

REFERENCES

1. Tanabe K., "Solid Acids and Bases: Their Catalytic Properties." Kodansha and Academic Press, Tokyo/New York/London, 1970.
2. Amato I., Martorama D., and Sliengo, B., *in* "Sintering and Catalysis" (G. C. Kuczynski, Ed.), p. 187, Plenum, New York, 1975.
3. Murrel, L. L., Dispenziere, N. C., Jr., and Kim, K. S., *Catal. Lett.* **2**, 263 (1989).
4. Niwa, M., Katada, N., and Murakami, Y., *J. Phys. Chem.* **94**, 6441 (1990).
5. Katada, N., Ishiguro, H., Muto, K., and Niwa, M., *Adv. Mater., Chem. Vap. Deposition* **1**, 54 (1995).
6. Katada, N., Toyama, T., and Niwa, M., *J. Phys. Chem.* **98**, 7647 (1994).
7. Katada, N., and Niwa, M., *Res. Chem. Intermed.* **24**, 481 (1998).
8. Katada, N., and Niwa, M., *Adv. Mater., Chem. Vap. Deposition* **2**, 125 (1996).
9. Fripiat, J. J., and Uytterhoeven, J., *J. Phys. Chem.* **66**, 800 (1962).
10. Peri, J. B., *J. Phys. Chem.* **69**, 211 (1965).
11. Knözinger, H., and Ratnasamy, P., *Catal. Rev. Sci. Eng.* **17**, 31 (1978).