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# Synthesis of a ceramic acid of tungstated alumina more active than silica-alumina for decompositions of cumene, ethylbenzene, and toluene

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A ceramics acid, calcined at temperatures above 1000 °C, was obtained by impregnating aluminum hydroxide with aqueous ammonium metatungstate followed by calcining in air at 1000–1200 °C (1–5 wt% W); its acidity and catalytic activity for decompositions of toluene, ethylbenzene, and cumene are higher than those of silica-alumina.

**KEY WORDS:** $WO_3/Al_2O_3$; Ar adsorption; Ceramic acid; Cracking; Cumene; Ethylbenzene; Toluene.

Ceramics are made by calcination of inorganic materials at a high temperature and favorably impressed upon stability. Among those materials, brick is a typical example, usually produced by calcination at temperatures above 1000 °C.

Solid acids such as alumino-silicates and binary oxides, whose typical examples are $SiO_2$–$Al_2O_3$ and $TiO_2$–$ZrO_2$, are usually prepared by calcination at 500–600 °C [1–3]; the treatment at higher temperatures reduces the surface acidity as well as catalytic activity.

We have prepared a new solid acid whose preparation was brought by calcination in the temperature range for preparation of ceramics, ≥1000 °C. The preparation is simple, and the point is usage of a small quantity of tungsten and of alumina gel. Tungstated-alumina is obtained by calcination in air at 1000–1200 °C after impregnating alumina with aqueous metatungstate. The materials show remarkable surface-acidities and activities for acid-catalyzed reactions, higher than silica-alumina, with fairly high acidity on the surface. As a stable material just like brick, the prepared ceramics was quite stable as a solid acid.

Metastable aluminas such as $\gamma$-alumina are widely used as catalyst and the catalyst support in industry. A great variety of transition aluminas are converted into the inactive $\alpha$-alumina by heat-treatment at temperatures above 500–1200 °C [4]. New acid sites are developed on the surface of alumina by introducing tungsten oxides [5, 6]; calcination at a high temperature is effective to develop the acid sites, but the optimum calcination temperature is 700 °C, at the highest.

This is the first to synthesize a solid acid with high acidity on the surface of alumina obtained by calcination in the ceramics range for preparation, and the work is highly related to green chemistry. Here, we report the preparation method of a new ceramics acid.

The catalyst ($WO_3/Al_2O_3$) was prepared by drying aluminum hydroxide (Koujundo Kagaku, Ltd., commercial grade, powdered below 100 mesh) at 100 °C followed by impregnating with aqueous ammonium metatungstate [$(NH_4)_6(H_2W_{12}O_{40})$, Nippon Inorganic Color & Chemical Co.], evaporating water, drying, and calcining in air for 3 h. The concentration was 1 wt% W (1.18 wt% after calcination at 1200 °C), 3 wt% W, and 5 wt% W (4.43 wt% after calcination at 1000 °C) based on the hydroxide, denoted as 1%-$WO_3/Al_2O_3$, 3%-$WO_3/Al_2O_3$, and 5%-$WO_3/Al_2O_3$, respectively.

Silica-alumina was supplied from the Catalysis Society of Japan as a reference catalyst and calcined at 500 °C: JRC-SAL-2 (surface area, 560 $m^2/g$). $Al_2O_3$ was obtained by calcination of the hydroxide at 1000 or 1200 °C. All of the catalysts were calcined in air for 3 h and powdered to below 100 mesh.

Reactions of alkylbenzenes were carried out in a microcatalytic pulse reactor as described elsewhere (flow rate of He carrier gas 30 ml/min; pulse size 1 $\mu$l) [7]. Effluent products were directly introduced into a gas chromatographic column for analysis (Bentone 34 + DIDP, 2 m, 80–100 °C). The catalyst was again heated at 300 °C for 1 h in the He flow before reaction. Activities were compared with the first pulse value.

The heat of Ar adsorption was determined by measuring the adsorption isotherm of Ar by means of a volumetric method using a conventional BET system. The adsorption temperature was controlled at −30 – −60 °C, along with a pressure of 2–100 kPa.

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A ceramics acid was obtained by impregnating aluminum hydroxide with aqueous ammonium metatungstate followed by calcining in air at temperatures above 1000 °C (1–5 wt% W) and examined in several acid-catalyzed reactions. First, the cracking of cumene into benzene and propylene was carried out with a small portion of catalyst at 250 °C, low compared with an usual temperature for the reaction; the results are shown in figure 1 as a function of calcination temperature of the 5 and 1% W-added catalysts. The highest activity was observed with calcination at 1000 and 1200 °C for the 5 and 1% impregnated materials [5%-$WO_3/Al_2O_3$ (1000 °C), 1%-$WO_3/Al_2O_3$ (1200 °C)], respectively. The 1%-$WO_3/Al_2O_3$ catalyst was tested for the reaction at higher temperature, 300 °C; the calcination temperature showing the highest activity was really 1200 °C. When the proportion of W in the catalyst was 3%, the curve showing the conversions with the calcination temperature over the catalyst was an intermediate state between the 1 and 5% materials, indicating the highest activity with calcination at 1100 °C.

Reactions were carried out for the less reactive ethylbenzene and the least reactive toluene among alkylbenzenes with 0.2 g of catalyst at 280 °C and with 0.5 g at 350 °C, respectively. The results are shown in table 1 together with those for $SiO_2$–$Al_2O_3$ for comparison and with their conversions of cumene. The present catalysts, 5%-$WO_3/Al_2O_3$ (1000 °C) and 1%-$WO_3/Al_2O_3$ (1200 °C), showed the activities higher than those of $SiO_2$–$Al_2O_3$ for the decomposition of ethylbenzene to benzene and ethylene and for the disproportionation of toluene to benzene and xylenes. Although the activities of 3%- and 5%-$WO_3/Al_2O_3$ calcined at 1100 and 1000 °C, respectively, for cumene were higher than that of $SiO_2$–$Al_2O_3$, that of 1%-$WO_3/Al_2O_3$ (1200 °C) was lower. It is indicative that the latter sample heat-treated at the quite high temperature holds little amounts of the acid-strength suitable for the reaction of cumene on the surface with the much small surface area described in the next section. Aluminas without the tungstate calcined at temperatures above 1000 °C were inactive at all for the three reactions.

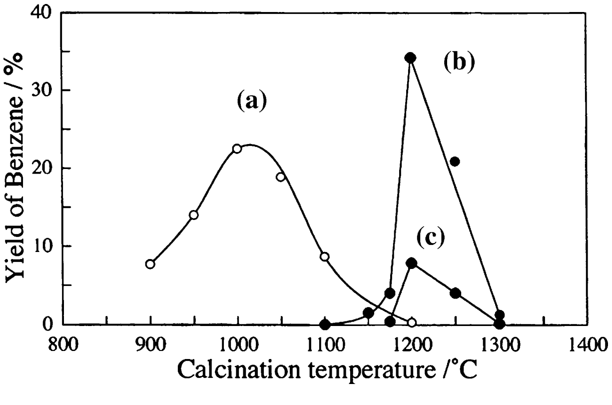

Figure 1. Catalytic activities of 5%-$WO_3/Al_2O_3$ (a) and 1%-$WO_3/Al_2O_3$ (b, c) for the cracking of cumene to benzene and propylene at 250 °C (a, c) and 300 °C (b) (0.05 g catalyst).

Table 1
Comparison of the activities of $WO_3/Al_2O_3$ with those of silica-alumina for reactions of alkylbenzenes

| Catalyst | Conversion (%) | | |
|---|---|---|---|
| | Toluene[a] | Ethylbenzene[b] | Cumene[c] |
| $Al_2O_3$ (1000 °C) | 0 | 0 | 0 |
| $Al_2O_3$ (1200 °C) | | | 0 |
| 1%-$WO_3/Al_2O_3$ (1200 °C) | 0.6 | 1.3 | 7.9 |
| 3%-$WO_3/Al_2O_3$ (1100 °C) | | | 12.3 |
| 5%-$WO_3/Al_2O_3$ (1000 °C) | 8.7 | 3.9 | 22.5 |
| $SiO_2$–$Al_2O_3$ | 0.1 | 0.4 | 10.8 |

[a] Reactions with 0.5 g of catalyst at 350 °C.
[b] Reactions with 0.2 g of catalyst at 280 °C.
[c] Reactions with 0.05 g of catalyst at 250 °C.

Specific surface areas of 5%-$WO_3/Al_2O_3$ (1000 °C) and 1%-$WO_3/Al_2O_3$ (1200 °C) were 30.2 and 7.7 $m^2/g$, respectively, compared with 4.8 $m^2/g$ for $Al_2O_3$ (1200 °C), indicating increase of the area by the addition of W.

Analysis of the surface acidity using Ar as a probe was performed. There exist problems when temperature-programmed desorption (TPD) technique is applied to solid acids with high acidity by using probes such as ammonia and pyridine. Ar was found to be applicable as a probe [8, 9]. The adsorption heat was calculated from a temperature dependence of amount of Ar adsorption at temperatures from −30 to −60 °C to be −16.4 and −14.7 kJ/mol for 5%-$WO_3/Al_2O_3$ (1000 °C) and 1%-$WO_3/Al_2O_3$ (1200 °C), respectively, compared with −14.4 kJ/mol for $SiO_2$–$Al_2O_3$ [10, 11]. Thus, the acid strength of the both catalysts is higher than that of $SiO_2$–$Al_2O_3$; the strength is in harmony with the activities for decompositions of alkylbenzenes.

To the best of our knowledge this is the first synthesis of a ceramics acid with fairly high acidity on the surface of alumina, its acidity being higher than that of silica-alumina. The materials are obtained by calcining aluminum hydroxide impregnated with ammonium metatungstate (1–5 wt% W) at 1000–1200 °C in air. Solid acids calcined at temperatures above 1000 °C are termed "ceramics acid".

## References

[1] A. Corma, J. Martinez-Triguero, S. Valencia, E. Benazzi and S. Lacombe, J. Catal. 206 (2002) 125.
[2] W. Zhang, X. Han, X. Liu and X. Bao, Macropor. Mesopor. Mater. 50 (2001) 13.
[3] K. Tanabe, in *Catalysis-Science and Technology*, (eds.) Vol. 2, J.R. Anderson and M. Boudart (Springer-Verlag, Berlin, 1981).
[4] M. Digne, P. Sautet, P. Raybaud, H. Toulhoat and E. Artacho, J. Phys. Chem. B 106 (2002) 5155.
[5] S.L. Soled, G.B. McVicker, L.L. Murrell, L.G. Sherman, N.C. Dispenziere Jr., S.L. Hsu and D. Waldman, J. Catal. 111 (1985) 286.

[6] S.R.G. Garrazàn, C. Martin, G. Solana and V. Rives, Langmuir 17 (2001) 6968.
[7] M. Hino and K. Arata, Chem. Commun. (1995) 789.
[8] H. Matsuhashi and K. Arata, Chem. Commun. (2000) 387.
[9] H. Matsuhashi, T. Tanaka and K. Arata, J. Phys. Chem. B 105 (2001) 9669.
[10] H. Matsuhashi and K. Arata, Phys. Chem. Chem. Phys. 6 (2004) 2529.
[11] H. Matsuhashi and K. Arata, Catal. Survay Asia (in press).