High Acidity of Silica–Titania and its High Catalytic Activity for Amination of Phenol with Ammonia

By KOZO TANABE,* MASAYOSHI ITO, and MASAAKI SATO

(Department of Chemistry, Hokkaido University, Sapporo, Japan)

Summary A new mixed oxide, SiO_2–TiO_2, prepared by a coprecipitation method showed a surprisingly high acidity and higher catalytic activity and selectivity for the title reaction than SiO_2–Al_2O_3.

MIXED oxides, TiO_2–ZnO[1] and SiO_2–ZnO[2], show high surface acidity and catalytic activity for the hydration of ethylene and the isomerization of but-1-ene, respectively. We report the acidic properties and the catalytic activity of SiO_2–TiO_2.

The SiO_2–TiO_2 catalysts of several compositions were prepared as follows. Mixtures of hydroxides were coprecipitated by adding 28% aqueous ammonia to an aqueous solution of ethyl silicate and titanium tetrachloride until the pH of the solution becomes 7·5 and then washing thoroughly with water. The coprecipitated hydroxides were then calcined at 500° for 3 h after drying at 100° for 20 h. Single oxides, SiO_2 and TiO_2 were prepared similarly as above. Silica–alumina used for comparison was a reagent of Nikki Chem. Co. which contained 15% (by weight) of Al_2O_3. The acidity and acid strength of the catalysts were measured by titration with n-butylamine, using *p*-dimethylaminoazobenzene (pK_a = + 3·3), benzeneazodiphenylamine (pK_a = + 1·5) and dicinnamalacetone (pK_a = − 3·0) as indicators. The amounts of ammonia and n-butylamine adsorbed on the mixed oxides at various temperatures were measured by using a microbalance. Specific surface areas of the catalysts calcined at 500° were

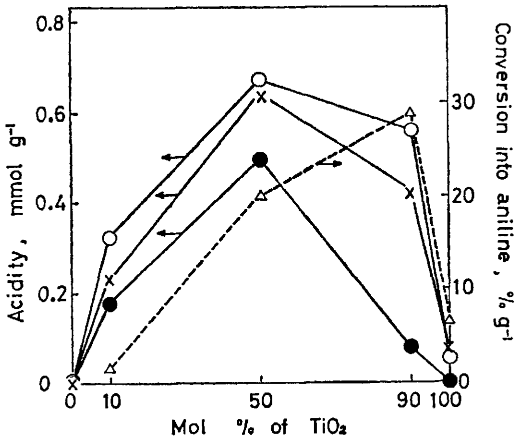

FIGURE. *Acid amounts at different* pK_a's *and catalytic activities of* SiO_2–TiO_2 *of various compositions.* ○; pK_a = + 3·3, ×; pK_a = + 1·5, ●; pK_a = − 3·0, △; *catalytic activity.*

determined by applying the B.E.T. method to the adsorption isotherm of nitrogen at −196°.

The amination reaction was carried out at 450° by using an ordinary flow method. The mol ratio of phenol to ammonia was 9:1. A conversion percent of phenol at a contact time of 22·7 g h mol^{-1} and a reaction time of 60 min was taken as a catalytic activity. Aniline and diphenylamine were analysed by g.c. with a column of silicone DC 500 or nylon 6.

The acidities at various acid strengths of the catalysts are shown in the Figure. The maximum acidities at pK_a +3·3, +1·5, and −3·0 observed for SiO_2–TiO_2 of mol ratio 1:1 were higher than the acidity (0·4 mmol g^{-1}) of SiO_2–Al_2O_3. The amounts of ammonia and n-butylamine that remained on SiO_2–TiO_2 (mol ratio = 1:1) after evacuation at 450° were 1·3 and 1·0 mmol g^{-1}, respectively, compared to 0·9 and 0·4 mmol g^{-1} for SiO_2–Al_2O_3. SiO_2–TiO_2 (1:1 or 1:9) changed even the basic colours of benzalacetophenone (pK_a = − 5·6) and anthraquinone (pK_a = − 8·2) to their acidic colours. Thus, it is evident that SiO_2–TiO_2 (1:1 or 1:9) has strong acid strength as well as high acidity. Since specific surface areas of SiO_2, SiO_2–TiO_2 (9:1, 1:1 or 1:9), and TiO_2 are 227, 292, 338, 245, and 84·9 m^2 g^{-1}, respectively, the change in acidic property by mixing each oxide is partly due to the change in surface area, but the acidities per unit surface area of SiO_2–TiO_2 are much larger than those of single oxides. It should be noted that the *X*-ray diffraction diagrams of SiO_2–TiO_2 (1:1) gave no diffraction lines indicating its amorphous form.

The catalytic activity of SiO_2–TiO_2 changed depending on the composition as shown by a dotted line in the Figure. The conversion of phenol into aniline at reaction time of 60 min was 29% g^{-1} of catalyst for SiO_2–TiO_2 (1:9), compared to 22% g^{-1} for SiO_2–Al_2O_3. The activity per unit surface area of SiO_2–TiO_2 (1:9) was larger than that of TiO_2. The yield of diphenylamine was 0·8% for SiO_2–TiO_2 compared to 1·3% for SiO_2–Al_2O_3. Benzene (less than 0·5%) was formed after 105 min.

(*Received*, 30*th May* 1973; *Com.* 761.)

---

[1] K. Tanabe, C. Ishiya, I. Matsuzaki, I. Ichikawa, and H. Hattori, *Bull. Chem. Soc. Japan*, 1972, **45**, 47

[2] K. Tanabe, T. Sumiyoshi, and H. Hattori, *Chem. Letters*, 1972, 723.