Role of the precipitation device on the properties of Al_2O_3 – TiO_2 mixed oxides
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Role of the Precipitation Device on the Properties of Al_2O_3-TiO_2 Mixed Oxides

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Abstract

The quality of Al_2O_3-TiO_2 mixed oxides produced in continuous mode by using two original rapid mixers (the impinging jets and the sliding surface mixing device) as precipitation reactors is compared with one obtained by a standard stirred tank. The properties of agglomerate particles strongly depend on the operating conditions and particularly on the type of precipitator used for their production.

Keywords: co-precipitation, mixed oxides, alumina, titanium dioxide, rapid mixers

1. Introduction

It is recently proved that Al_2O_3-TiO_2 mixed oxides could be excellent catalysts for many important industrial processes (Pophal et al. 1997, Lecrenay et al. 1998, Miller and Lakshmi 1999, Segawa et al. 2000, Reddy et al. 2001, Macleod et al. 2004). Several routes exist to produce them. For example, mixing of Al_2O_3 and TiO_2 powders in suspension (Bueno et al. 2005), or mixing of an ammonium aluminium sulphate solution and a TiO_2 powder (Liu et al. 2005), with subsequent calcinations in both cases, can be quoted. Another method consists in co-precipitation from an aluminium salt (sulphate or nitrate) and an inorganic or organic soluble compound of titanium, for example isopropyl ortho-titanate or titanium tetrachloride (Maity et al. 2003, Hernandez and Bautista 2005). Lastly, sol-gel processes (Farias et al. 2003, Wunderlich et al. 2004, Hernandez and Bautista 2005) can also be employed.
A cost-effective way to produce alumina catalyst is to precipitate AlOOH by mixing of sodium aluminate and aluminium sulphate solutions (Rousseaux 2000). We have chosen this route to produce Al_2O_3-TiO_2 mixed oxides by substituting the solution of aluminium sulphate by the titanyl sulphate solution. It was earlier shown (Rousseaux et al. 2000, Bénet et al. 2002) that the properties of agglomerate particles of boehmite strongly depend on the type of precipitation device used for producing them, so the aim of this work is to study the role of the type of precipitation reactor on the quality of Al_2O_3-TiO_2 mixed oxides in order to obtain a catalyst with controlled end-use properties. In this context, three types of precipitation reactors are used. The first one is a standard reactor equipped with a Rushton turbine. The two others

are original rapid mixers: the impinging jets (Bénet et al. 2002) and the sliding surface mixing devices (Rousseaux et al. 1999).

2. Materials and methods

The experimental setup is composed of two tanks feeding the precipitator thanks to pumps (Fig.1). Neutralization between sodium aluminate and titanyl sulphate is carried out at 70°C. The concentrations of both solutions are chosen in such a way that the final suspension at the outlet of the precipitator contains 60 g.L^{-1} of solid phase and pH = 9. Two different Al_2O_3-TiO_2 catalysts are produced: the first one is composed of 10%, while the second one contains 30% of TiO_2.
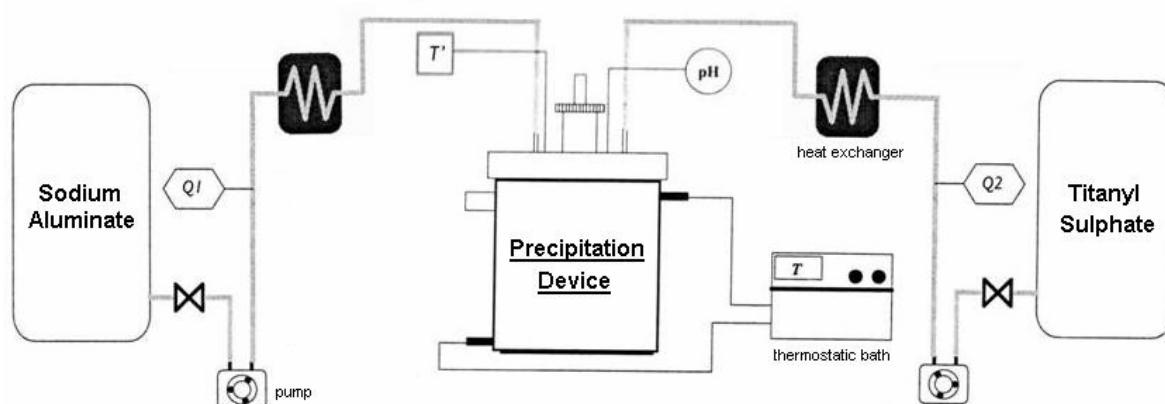

Figure 1: Experimental setup

The reactor used as a reference in this study is a Continuous Stirred Tank Reactor (CSTR) of 2.5 liters in volume equipped with four baffles. The Rushton turbine is 50 mm in diameter and it rotates at 1000 rpm. The feed points are located in the discharge stream of the impeller, where the specific energy dissipation is the highest. As previously mentioned, we compared the properties of Al_2O_3-TiO_2 mixed oxides produced by this reactor with two other precipitators: impinging jets and sliding surface mixing devices. The impinging jets technology (IJ) is schematically represented in Figure 2. This device enables a very close contact between reactants entering the precipitator thanks to two facing tubes. Impaction between both jets creates a very small mixing volume (Bénet et al. 2000), where supersaturation level is very high and confined only by the environmental fluid in the tank avoiding in this manner scaling phenomena. Tubes are 36 mm spaced, and nozzles are 2 mm in diameter. Consequently, the velocity of injected fluids is between 1 and 4 m.s^{-1} depending on the chosen mean residence time inside the precipitator. The impinging jets device shown in Figure 2 is submerged in the stirred tank and located at the level of the discharge stream of the Rushton turbine.

Another alternative for obtaining the high intensity of mixing is the use of sliding surface mixing device (SSMD) also named rotating disc reactor (Fig. 3). This precipitator has already shown its advantages in previous studies (Rousseaux et al. 1999, Rousseaux et al. 2001). It can be approached as combination of two separate zones: the confined volume situated under the disc, where reactive solutions are injected under a very high shear rate and agglomerated particles are produced, and the upper zone of the tank, more poorly mixed by the disc, where

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ripening of agglomerates takes place. Our disc is situated 2 millimetres from the bottom of the reactor and its rotating speed reaches 3000 rpm.
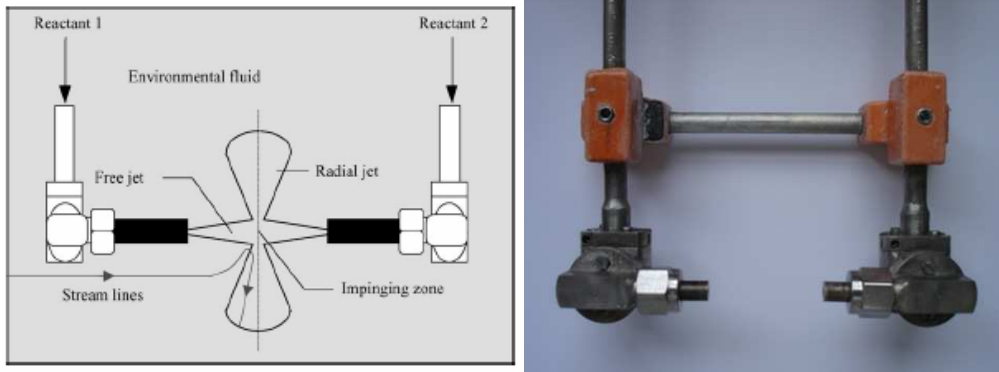

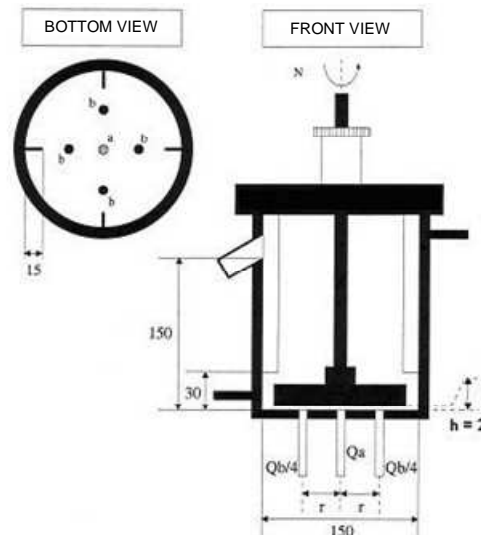Figure 2: Scheme of the impinging jets mixing device

Figure 3: Scheme of the sliding surface mixing device

The experiments have shown that in all cases very porous agglomerates are obtained. Their end-use properties are judged through several parameters, such as particle size distribution, specific surface area, porosity and pore size distribution, and homogeneity of mixed oxide particles. The particle size distribution is measured with a Malvern Mastersizer S particle analyzer. Specific surface area and porosity are determined from sorption isotherms obtained by Sorptomatic 1990 of Thermo Electron Corporation, while the homogeneity of TiO_2 distribution into Al_2O_3 matrix is checked by X-ray microanalysis in a scanning electron microscope JEOL JSM-T 330 A.

3. Results

The influence of principal operating conditions is experimentally studied. The first one is the mean residence time τ varying from 2 to 20 minutes. Another interesting parameter is the final respective proportion of Al_2O_3 and TiO_2 species into the mixed oxides. As described above,

two kinds of catalysts are produced: the first one is composed of 10 % of TiO_2 and 90 % of Al_2O_3, while the second one contains 30 % of TiO_2 and 70 % of Al_2O_3.

Figure 4 shows the mean particle size as a function of the type of precipitator, mean residence time and species proportion. First of all, it is clearly proved that the quantity of TiO_2 does not influence the size of agglomerates. On the contrary, the reactor geometry is a decisive factor.
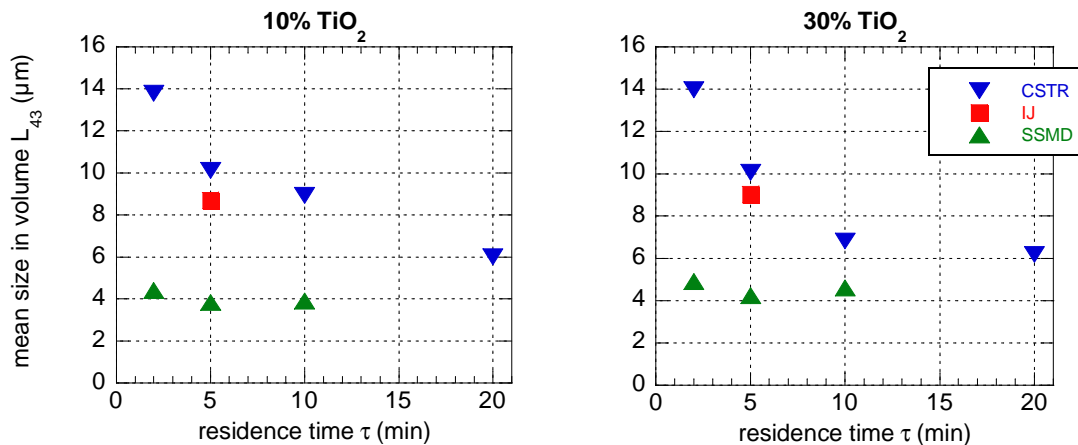

Figure 4: Influence of the precipitation device and operating conditions on the mean particle size

The mean size of agglomerates obtained by the CSTR is smaller than the Kolmogorov scale, which is here equal to 24 µm. Despite, L_{43} decreases when residence time τ increases. It can be explained by the fact that for short residence times, supersaturation is more important. This gives very high nucleation rates and then, numerous elementary particles. Since the agglomeration rate is proportional to the square of the number of particles, the shorter the residence time is, the bigger the agglomerates are. In addition, specific surface area variation as a function of mean residence time, shown in Figure 5, proves that the elementary particles are all more numerous and finer as τ is small.

In the case of the SSMD, the mean particle size is independent of the mean residence time, because in this reactor a very high shear rate value (the same for all experiments, nearly 6000 s^{-1}) is mechanically produced. For this reason, the intensity of mixing depends only on the shear rate, but not on the mean residence time.
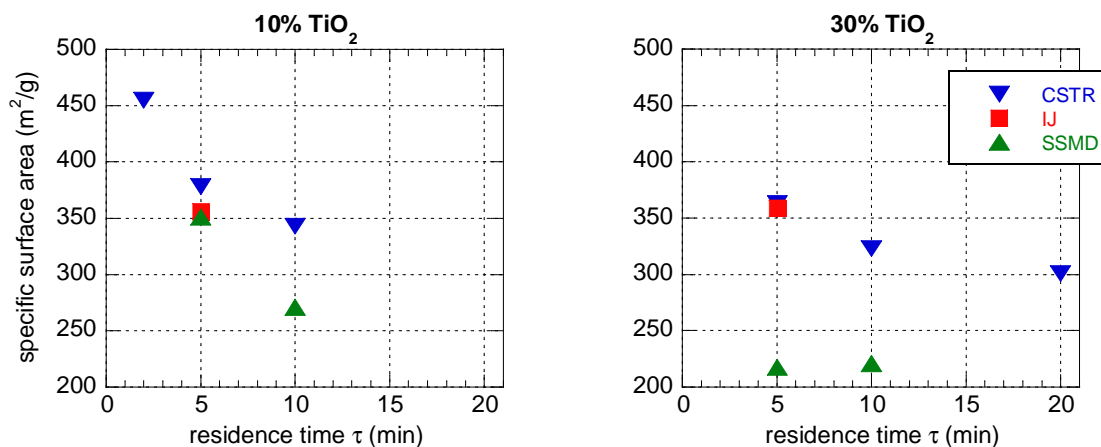

Figure 5: Influence of the precipitation device and operating conditions on the specific surface area

Only one point appears on Figure 4 for the impinging jets, at τ = 5 min. Nevertheless, other residence time values have been tested with this device, 2 minutes in particular, but the corresponding results are not significant for 10% of TiO_2 as well as for 30% one. The extremely high nucleation rate in a small volume caused by the rapid mixing of reactants (the jet velocities are high, so consequently, the intensity of mixing is high) is certainly responsible of formation of an amorphous solid. Then, the action of Rushton turbine, in spite of its high stirring speed of 1000 rpm, cannot rapidly mix this part of reaction volume with the surrounding fluid in the reactor in order to avoid the gel formation.

Figure 6 shows the scanning electron microscopy photographs of precipitates produced by the three reactors, where it can be qualitatively observed that different structures are obtained. On the contrary, the homogeneity of TiO_2 distribution in the Al_2O_3 matrix obtained by X-ray cartography (not shown here) is excellent (Mouret 2005).
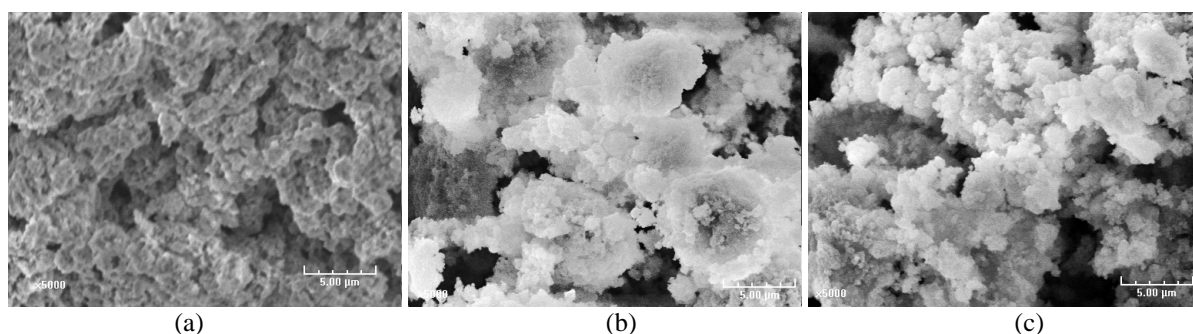

| (a) | (b) | (c) |

Figure 6: Scanning electron microscopy photographs of agglomerate particles produced by: a) the classical stirred tank reactor, b) the classical stirred tank reactor equipped with an impinging jets device, c) the sliding disc mixing device

Specific surface area and porosity are the key parameters for catalysis. In accordance with Figure 5, for any precipitation device, specific surface area of 10% TiO_2 mixed oxide seems to be slightly higher than this one of 30% TiO_2. Generally, the specific surface area decreases as the mean residence time increases, because (as mentioned above) with the increasing of mean residence time, the nucleation rate is lower and, consequently, the size of elementary particles is bigger. In particular, the sliding surface mixing device appears here to be the less interesting reactor giving the lowest specific surface area. In addition, for a mean residence time of 2 min, it produces an amorphous solid with a specific surface area less than 10 m^2g^{-1} (not represented in Fig. 5) in spite of the same treatment methodology (filtration, washing, drying, etc.) used after the precipitation of all catalyst precursors.

For all products, the porosity is about 60%. In the case of Al_2O_3-TiO_2 mixed oxides used as catalysts, the mesoporosity is a matter of first importance. Under the same operating conditions, the mesoporosity attains the highest value when the impinging jets mixing device is used (see Fig. 7). Al_2O_3-TiO_2 mixed oxides obtained with the impinging jets mixing device have a mesoporosity of 85 % in relation to the total porosity, whereas ones produced by the classical stirred tank or by sliding surface mixing device have only 65% in average. In addition, it is curiously to note that, on the contrary to other precipitators, in the case of the impinging jets, the mixed oxide containing 30 % of TiO_2, has a mesoporosity higher than this one containing 10 % of TiO_2. These experimental observations represent very important

information showing that different precipitation devices can produce solid mixed oxides whose properties as catalysts can differ in large intervals.
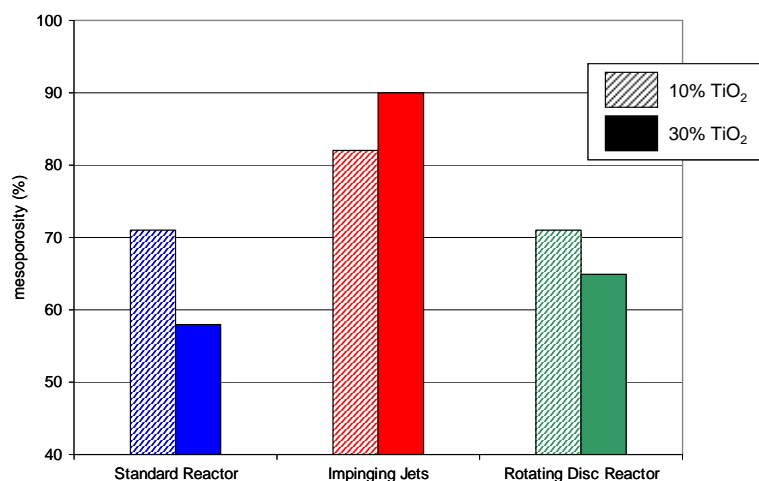
Figure 7: Mesoporosity (in % of the total porosity) obtained by different reactor geometries in the case of mean residence time of 5 min.

4. CONCLUSIONS

Numerous published papers study the influence of physicochemical conditions on the properties of catalysts and catalyst supports containing alumina, but the role of the precipitation device for producing them is almost totally ignored. Recently, Rousseaux (2000) and Rousseaux et al. (2000) have carried out many experiments under the same physicochemical conditions and clearly showed that the choice of the process technology was a determining factor for controlling the end-use properties of obtained products. An analogous situation exists in the case of mixed oxides Al_2O_3-TiO_2 obtained by co-precipitation. This work shows for the first time that the precipitator type sensibly influences the quality of this kind of catalyst. The classical stirred tank, equipped or not with an impinging jets mixing device, gives higher specific surface area then the sliding surface mixing device, especially in the case of low mean residence time values. The most important parameter making the difference between the produced mixed oxides is mesoporosity. According to this criterion, the classical reactor equipped with the impinging jets mixing device produces the catalysts of highest quality having simultaneously high specific surface area and high mesoporosity.

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