TEAMCAT Solutions

SPEED UP YOUR CATALYSIS

Characterization of the acid-base properties of solid materials with isopropanol probe

MULTI-R® G-4100

MULTI-C® 8100

In partnership with

SAINT-GOBAIN

Application note: AN001

02/2018 V1.0

Contact: Teamcat Solutions, Centrale Lille, Cité Scientifique, 59650 Villeneuve d'Ascq - France

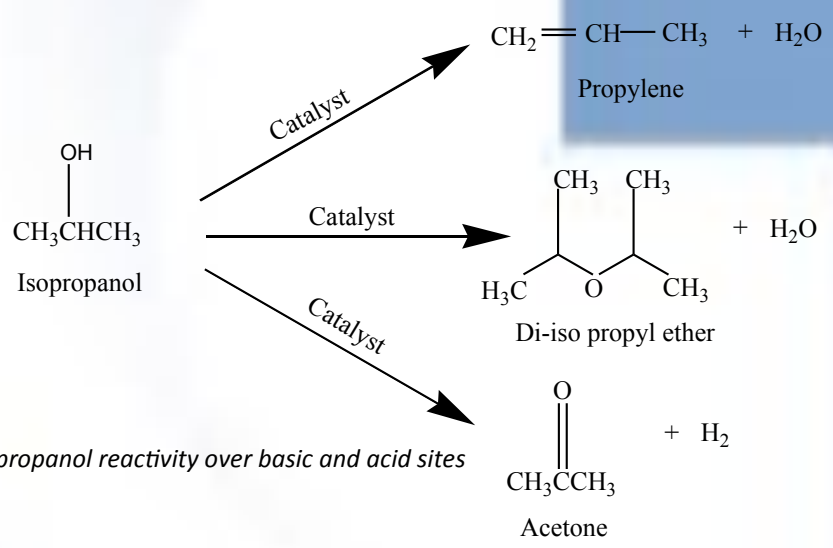
jdelaux@teamcat-solutions.com | http://teamcat-solutions.com | +33 6 31 79 27 62 | +33 3 20 33 53 55

Application note

Characterization of the acid-base properties of solid materials with isopropanol probe

Principle

The Multi-R® of the TEAMCAT SOLUTIONS company is a multi-reactor system. It has been basically designed for the measurements of **catalytic performances** of powdered solids, in the gas phase, in four parallel continuous flow reactors. In addition, it also can be used to conduct test reactions to **characterize the surface acid-base properties** of powdered solids loaded in the Multi-R® reactors catalytic or not. The **dehydration of isopropanol** (*Scheme 1*) is a reaction often used for this purpose, especially for characterizing the **properties of metal oxides**.[1] In fact, depending on the level of conversion of the isopropanol under specific conditions, it is possible to **characterize the activity of the studied solid**. The selectivity to **propylene (PEN) or acetone (AC)**, depending on the followed reaction pathway, will be an indication of the nature of the sites, respectively acidic and basic. It is also possible to form **di-iso propyl ether (DIPE)** by condensation of two molecules of ethanol over acid sites.



Scheme 1: *Isopropanol reactivity over basic and acid sites*

Experimental conditions

Twelve solids supplied by Saint-Gobain Norpro (silica, zirconia, titania and alumina which references begin by SS, SZ, ST and SA, respectively) were previously ground and sieved between **100 and 200 µm** before being calcined under airflow in a **TEAMCAT SOLUTIONS Multi-C® oven at**

400 °C (temperature ramp 10 ° C / min) during **15 h** to clean up their surface. This pretreatment is important for the good stability of the solids and the reliability of the results.

As far as possible, for each test, the isopropanol **conversion** was adjusted in order to remain **below 10%** (differential conditions enabling reliable evaluation of the kinetic parameters) by adjusting the reaction temperature.

The selectivities to each product products (PEN, AC and DIPE) were calculated as well as **the carbon balance**. This latter was always larger than 95%, wich is considered as a

Operating conditions:

- **Particule size: 100-200 µm**
- **Solid weight: 80 mg**
- **Atmospheric pressure**
- **Gas: Air + 1% isopropanol (using a saturator)**
- **Flow rate: 20 mL/min**

Table 1: Experimental data collected for one of the samples (SZ 61143)

$T_{reactor}$ (°C)	Isopropanol conversion (%)	Carbon balance (%)	PEN selectivity (%)	DIPE selectivity (%)
90	0.2	100.0	0.0	86.2
95	0.9	99.4	0.0	34.5
100	2.1	98.7	14.3	25.6
105	3.3	98.1	15.8	25.0
110	3.6	98.0	17.4	26.3
115	5.9	97.3	24.6	29.9
117	7.6	96.3	24.7	27.1
119	8.5	95.6	23.5	25.1
122	9.0	95.6	25.0	25.9

[1]A. Gervasini, A. Auroux, *J. Catal.* 131, 190-198, 1991

The activation energies and the natural logarithms of the pre-exponential constants of the reactions were determined from the Arrhenius law plot (*Figure 1*) expressed as follows (*Table 2*):

$$\ln k = -\frac{Ea}{RT} + \ln A$$

In this case, the rate constant "*k*" can be likened to the reaction rate because of the zero order with respect to isopropanol. It is expressed in $mol.s^{-1}.m^{-2}$ and calculated as follows from the experimental data:

$$k = \frac{product\ concentration}{specific\ surface\ area * solid\ weight * contact\ time}$$

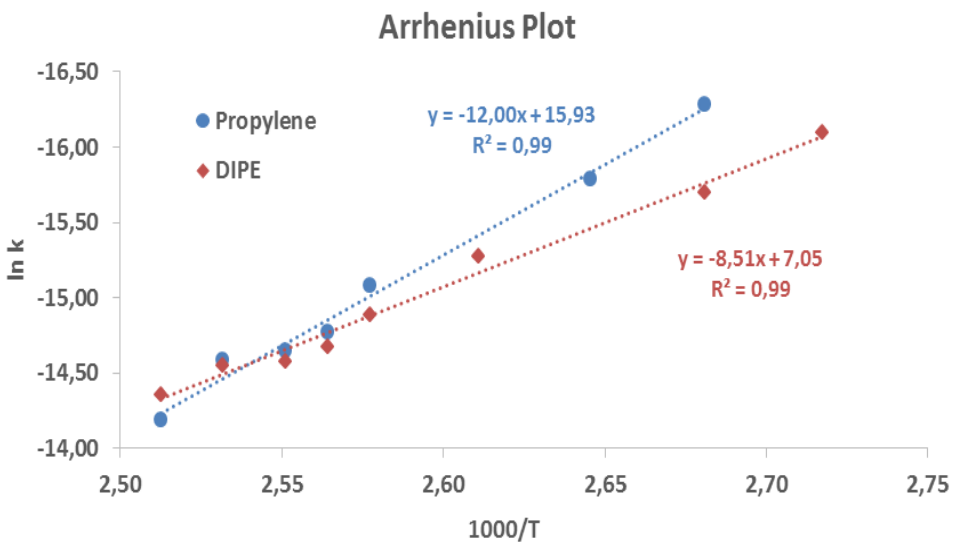


Figure 1: Arrhenius plot for SZ 61143

Table2: Kinetic parameters for SZ 61143

Sample	PEN		DIPE		Detected products
	Ea **(kJ/mol)**	***lnA***	***Ea*** **(kJ/mol)**	***lnA***	
SZ 61143	99.8	15.9	70.8	7.1	DIPE + PEN T>100°C

Results

The samples were tested under the same conditions while varying the temperature, as aforementioned. By using the previous formula, the obtained linear regression gave **coefficients of determination close to 0.99**. With these data, the following table (*Table 3*) was obtained. **The nature of the formed molecules, the temperature of their formation and the activation energies were determined for each solid.**

Table 3: Experimental data and kinetic parameters for all the solids

Sample	$T_{reactor}$ (°C)	PEN		DIPE		AC		Detected
		Ea (kJ/mol)	lnA	Ea (kJ/mol)	lnA	Ea (kJ/mol)	lnA	
SA 6178	140-178	137.0	22.0	121.2	16.5	-	-	DIPE + PEN
SA 6176	120-156	165.5	31.7	152.2	27.1	-	-	DIPE + PEN
SA 61169	150-180	143.6	22.7	108.6	12.2	55.6	-1.7	PEN + DIPE + AC T>160°C
SA 31132	160-210	104.6	12.8	49.5	-2.8	51.5	-2.4	PEN + DIPE T>175°C AC T>185°C
ST 61120	155-204	75.0	4.41	-	-	119.6	14.5	PEN et AC
SS 61138	190-265	118	12.1	-	-	147.7	16.5	PEN + AC T>250°C
SS 61137	215-285	64	-0.84	-	-	93.6	4.5	PEN + AC T>260°C
SS 61155	75-112	67.5	5.9	45.3	-2.9	-	-	PEN + DIPE T>90°C
SZ 61143	90-125	99.8	15.9	70.8	7.1	-	-	DIPE + PEN T>100°C
SZ 39140	160-212	52.1	-1.4	-	-	24.8	-9.0	PEN + AC T>180°C
SZ 61156	155-220	-	-	-	-	64.8	1.8	Only AC
SZ 61192	80-120	111.5	19.2	80.6	9.8	-	-	DIPE + PEN T>95°C

Samples	Specific surface area	Pore Volume (mL/g)
SA 6178	168	1.03
SA 6176	265	1.00
SA 61169	249	0.76
SA 31132	66	0.76
ST 61120	152	0.52
SS 61138	237	1.01
SS 61137	170	0.49
SS 61155	443	0.63
SZ 61143	119	0.29
SZ 39140	87	0.46
SZ 61156	122	0.23
SZ 61192	176	0.20

Table 4: Specific area and pore volume of the solids

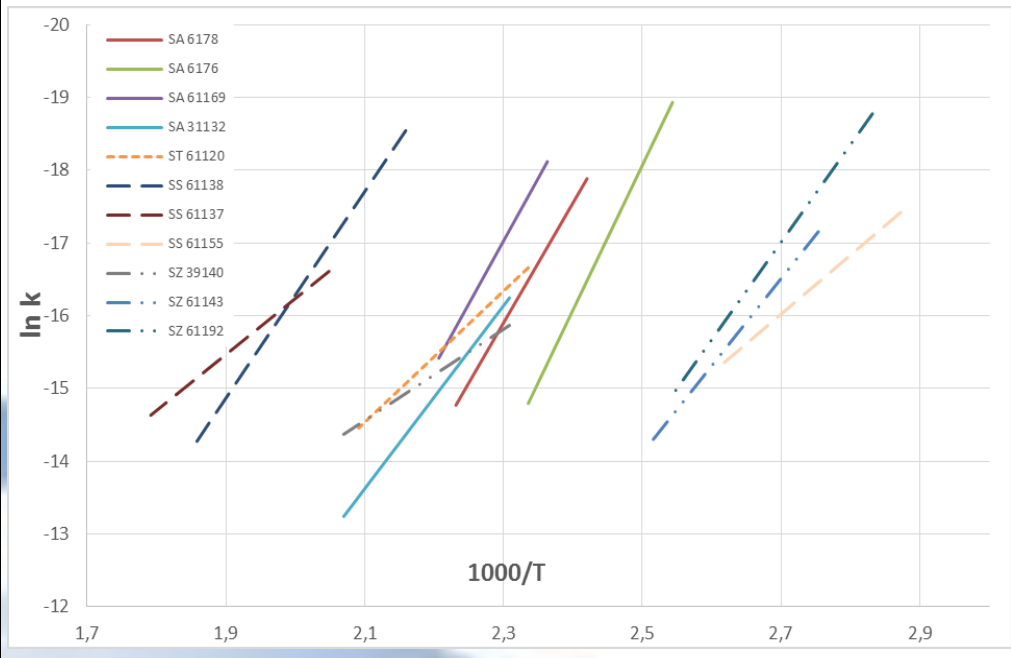


Figure 2: Arrhenius plots for convertion isopropanol to PEN for the different solids

It is considered that, if **PEN is formed, acid and/or basic** sites are present (dehydration reaction) while if **acetone is the only molecule** formed, the solids has **only basic sites** (dehydrogenation reaction). There is a direct relationship between the strength of the acidic sites and the activation energy (*Ea*) of the dehydration reaction. If the ***Ea* is** low, this suggests that there are **many and/or strong acid/basic sites** and the **dehydration will thus be easier**.

These results allow us **to sort the solids according to their reactivity**. Sorting the results according to the conversion of isopropanol to PEN, **we can indeeed classify** on the same graph **the different solids** using the Arrhenius law (*Figure 2*). In this study, SZ39140 and SZ 61192 and SS 61155 are the most active at low temperatures whereas SS 61138 and SS61137 require higher temperatures to observe a conversion of isopropanol to PEN. Regarding SZ 61156, only acetone is observed, wich indicates the absence of acid sites.

A fast and reliable method to characterize acid-base properties

The **surface acid-base properties** (*Table 4*) of a set of twelve solids from **Saint-Gobain Norpro** (silica, alumina, titania and zirconia materials) were studied by assessing the conversion reaction of isopropanol into propylene, acetone and di-iso propyl ether using the **TEAMCAT SOLUTIONS Multi-R® 4100**. The use of this high-throughput screening tool enable significantly reducing the time required to collect experimental data (**48 hours per solid** instead of one week on a conventional device with only one reactor) thanks to its four reactors working in parallel at different temperatures. The entire study therefore represents approximately **3 weeks of work against several months** with a conventional device. The collected data make it possible to highlight the different acid/base properties of the solids.

As a conclusion, this work confirms the possibility to use the **high-throughput technology to characterize solids**. Indeed, it provides very interesting informations **to sort the samples in various groups** according to their respective **acid-base properties**. Furthermore**, the time-saving** is the main **advantage** of using **Multi-R® 4100.**

To complete this study, other test reactions could be implemented in the Multi-R® 4100. Particulary with the **conversion of 2-methyl-but-3-yn-2-ol (MBOH)**, it would also be possible to **characterize the basic sites** of solids.

Contact : Teamcat Solutions, Centrale Lille, Cité Scientifique, 59650 Villeneuve d'Ascq - France
jdelaux@teamcat-solutions.com | http://teamcat-solutions.com | +33 6 31 79 27 62 | +33 3 20 33 53 55