Alkylation of benzene with isopropanol on β-zeolite: influence of physical state and water concentration on catalyst performances

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Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

Abstract

By using isopropanol as alkylating agent in the direct alkylation of benzene to cumene, under properly selected conditions, performances comparable to those afforded by the current industrial use of propylene have been obtained. The reaction is carried out in the presence of a β-zeolite-based catalyst. Catalytic performances are influenced by temperature and pressure at fixed benzene to isopropanol molar ratio. In particular, catalyst activity and catalyst deactivation rate depend on the water content in the liquid phase fraction of the reaction mixture, as predicted by state equations for LV equilibria in the reacting system. The successful use of isopropanol as alkylating agent has paved the road toward a viable acetone recycle in phenol production, as foreseeable in case of acetone/phenol unbalanced demand.
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1. Introduction

Cumene is the intermediate for the industrial production of phenol. The cumene route to phenol accounts for more than 90% of world phenol capacity. Benzene is first alkylated with propylene (C3-) to cumene. In a second step cumene undergoes oxidation to cumene hydroperoxide which is then submitted to an acid rearrangement step through which phenol and acetone are obtained.

The cumene process has been generally conducted by using, as a catalyst, a solid phosphoric acid on silica [1], a Friedel–Craft catalyst like aluminium chloride [2] or, more recently, zeolite-based catalysts. The processes based on solid phosphoric acid and aluminium chloride catalysts suffer from corrosion and environmental problems. Excellent results in cumene industrial production have been obtained by using a β-zeolite-based catalyst according to Polimeri Europa's cumene technology [3,4].

The co-production of phenol and acetone in a fixed ratio (0.61 kg of acetone per kg of phenol) may give rise to economic problems in case of an unbalanced market demand for the two products. Due to the rapidly growing market of phenol applications (mainly aromatic polycarbonate production) and parallel steady or declining market of acetone and its derivatives (e.g. methyl methacrylate via acetone cyanohydrin route), global phenol consumption is forecast to grow about twice than acetone up to 2010.

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Based on announced near-term new phenol capacities, an exceeding acetone supply of 600.000 tons per year is estimated in 2006, and more than 800.000 tons per year in 2010 [5].

Mitsui [6] has developed a cumene process in which propylene used as benzene alkylating agent is obtained from acetone reduction to isopropanol (IPA) and its subsequent dehydration. Direct alkylation of benzene with IPA would be a more cost effective solution, but the expected negative effects on catalyst performances and lifetime due to the presence of the high water quantities generated in the reaction mixture have to be faced.

In fact acid zeolite-based catalysts suffer from the presence of water, due to the highly hydrophilic character of zeolites which leads to a stable water adsorption during the reaction, lowering the catalyst performances.

Actually, with specific reference to β-zeolite, some attempts to overcome this problem by synthesising a zeolite showing a more hydrophobic character have been reported [7].

However, based on our experience and especially at very high water concentration in the reaction mixture, as it would be the case at an industrially convenient ratio between benzene and IPA, avoiding water adsorption phenomena through modification of the zeolite hydrophobic character appears to be scantly possible.

We have found that under properly selected reaction conditions, able to avoid negative water adsorption phenomena onto the catalyst, catalyst performances as good as those with pure propylene can be obtained [8,9].

The present work refers to the direct benzene alkylation with IPA by using the same PBE-1 proprietary β-zeolite-based catalyst as in Polimeri Europa's industrial cumene production technology.

2. Experimental

2.1. Catalytic materials and reactants

Pure H-β-zeolite, in powder form, has been used for preliminary batch catalytic tests. Proprietary PBE-1 β-zeolite-based catalyst, in pellet form, prepared starting from the above zeolite as a raw material, has been used for continuous catalytic tests.

The catalysts have been prepared in accordance to [10] experiment no. 2 for powder form zeolite and to [10] experiment no. 4 for pellet form PBE-1. The β-zeolite had a silica to alumina ratio (SAR) of 26.

Benzene and IPA were RPE pure reactants from Carlo Erba Reagenti while propylene with 99.9 % minimum purity was from SIO.

2.2. Apparatus and procedures for catalytic tests

2.2.1. Batch catalytic tests

A stainless steel autoclave with an internal volume of 500 ml is used. The required quantity of powder catalyst is first charged into the open autoclave. The autoclave is closed and the required quantity of benzene is charged by vacuum.

Agitation and heating are then turned on and, when the selected temperature has been reached, the right amount of liquid propylene or IPA is pumped into the autoclave. Nitrogen pressure is then applied up to 30 bar of total pressure. Reaction time starts just after completing the propylene or IPA loading.

2.2.2. Continuous catalytic tests

A micro-pilot plant is used. It consists of independent storage vessels and feeding pumps for benzene, propylene and IPA, a 20 ml tubular stainless steel reactor placed into an electric oven, a reactor effluent cooling unit and a collection system for liquid and gaseous reaction products.

The reactor is a stainless steel cylindrical tube of about 2 cm i.d. with a mechanical sealing system. A mobile temperature transducer is situated along the major axis of the reactor. The required reactor temperature and pressure are maintained, respectively, by a computer controlled electric oven and a reactor pressure discharge valve.

The reactor is charged with a catalyst quantity corresponding to a catalyst bed height of around 10 cm and with a small quantity of inert material put on top and bottom of the catalyst bed.

Pure benzene is fed at the required space velocity to the reactor until the reaction temperature has been reached, then propylene or IPA are fed at a space velocity corresponding to the required [benzene]/[IPA or C3-] ratio.

2.2.3. Analysis

The reaction products from batch and continuous tests are analysed by means of gas-chromatography using the following equipments and conditions for analysis of liquid products (1 and 3, respectively, for high and low concentration components) and gaseous products (2):

1. Carlo Erba GC 6000 gas-chromatograph equipped with a MEGA SE54 column with external diameter of 0.53 mm, length of 25 m and FID detector. Oven temperature program: 70 °C for 10 min isotherm, 3 °C/min up to 130 °C ramp, 10 °C/min up to 210 °C ramp, 210 °C for 20 min isotherm.
2. HP 6890 gas-chromatograph equipped with a PONA column with external diameter of 0.2 mm, length of 50 m and TCD detector. Oven temperature program: 35 °C for 4 min isotherm, 2 °C/min up to 70 °C ramp, 5 °C/min up to 220 °C ramp, 220 °C for 10 min isotherm.
3. Carlo Erba 4200 gas-chromatograph equipped with a Poropack-Q filled column with diameter of 4 mm, length of 2 m and TCD detector. Oven temperature program: 100 °C for 5 min isotherm, 10 °C/min up to 220 °C ramp, 220 °C for 5 min isotherm.

2.2.4. Physical state of the reaction mixture

The definition of the physical state of the reaction mixture, i.e. the relative amount of liquid and vapour phase, for continuous catalytic tests, as well as the calculation of water solubility are made by RKS state equation [11] whose interaction parameters are obtained from regression of experimental literature data for LV equilibria [12,13].

3. Results and discussion

3.1. Batch catalytic tests

A first set of catalytic experiments has been carried out in order to obtain a preliminary assessment of the general catalyst performances when IPA is used as a benzene alkylating agent (Table 1).

Table 1
Batch catalytic tests

	Reference	No.			
		1	2	3	4
Test conditions					
β-Zeolite powder (g)	2.0	4.0	4.0	4.0	4.0
Alkylating agent	Propylene	IPA	IPA + C3-	IPA	IPA
[C6]/[IPA or C3-]	7.2	7.3	7.3	7.2	7.1
[IPA]/[IPA + C3-] (%)	0	100	30	100	100
Reaction time (min)	60	240	240	240	240
Pressure (bar)	30	30	30	30	30
Temperature (°C)	150	150	150	170	190
Results					
Conversion (IPA or C3-) (%)	100.0	76.1	85.4	81.5	98.4
Selectivity [cumene]/[IPA or C3-] (%)	91.0	16.4	90.5	58.3	87.5
Selectivity [aromatics]/[IPA or C3-] (%)	99.0	16.5	95.3	60.2	94.6
Total water formed in reaction mixture (wt.%)	–	1.8	0.9	2.3	2.9
Calculated water solubility (wt.%)	–	1.8	1.8	2.7	4.1
Products distribution (wt.%)[a]					
Propylene	–	32.2	5.62	11.0	0.75
Diisopropylether	–	33.5	0.050	3.91	0.061
Cumene	94.0	33.8	88.8	82.2	92.9
Diisopropylbenzenes	4.26	0.15	3.02	1.73	4.85
Triisopropylbenzenes	1.06	0.013	0.17	0.052	0.25
Others	0.67	0.33	2.33	1.12	1.14

[a] On water free basis, without reactants.

The first column shows the results of a test with propylene (reference test). Selectivity [cumene]/[IPA or C3-] refers to the formed cumene on converted alkylating agent while selectivity [aromatics]/[IPA or C3-] refers to the sum of formed cumene + diisopropylbenzenes + triisopropylbenzenes on converted alkylating agent.

Test 1 showed that, keeping the reaction temperature and reactants molar ratio fixed to the values of the reference test, IPA was extensively, although not completely, converted. At the same time selectivities to cumene and aromatics remained considerably low, mainly due to the presence of unreacted intermediates, i.e. diisopropyl ether (DIPE) and propylene, among the products, even if the catalyst quantity had been increased two times and the reaction time up to four times. In other words, substantial IPA dehydration to DIPE and propylene was observed in test 1, while alkylation proceeded only at a quite limited extent. Therefore, it seems appropriate to relate the negative effect associated with the use of IPA as alkylating agent instead of propylene to the formation of water in the reaction system.

As a matter of fact, when the catalyst unloaded from test 1 was recovered, dried 3 h at 200 °C and re-utilised in the reference test, the same result already shown in Table 1 was obtained, thus confirming that the formed water was likely the reason for poor catalyst performances. This was further confirmed in test 2, carried out in the same conditions of test 1, but only partially substituting propylene with IPA, in order to reduce the amount of formed water: at a water concentration of 0.9 wt.% instead of 1.8 wt.% in the reaction mixture, a higher conversion and especially quite higher selectivity values were obtained; although total IPA conversion was still not achieved, selectivities became comparable to the reference test.

It can be calculated that the total amount of water that would be stoichiometrically formed in test 1, according to the fed composition, at full reaction advancement would largely overcome the solubility limit of water in benzene at the reaction conditions (1.8 wt.%).

On the contrary, total water actually formed in test 1 (1.8 wt.%) appears very close to this calculated solubility limit. We take this behaviour as an indication that, in addition to any likely effect of dissolved water in lowering catalyst activity, the presence of undis-

Table 2
Comparison of calculated water solubilities

Calculated water solubilities (wt.%)				
Test no.[a]	1	2	3	4
In benzene	1.3	1.3	2.7	4.1
In final reaction composition	2.0	1.9	2.9	4.1

[a] See Table 1.

solved water in the reaction mixture could possibly represent a barrier for the reaction advancement.

Water solubility in benzene is expected to match closely the solubility in the reaction system, since benzene is used in large excess as a reactant and represents the most abundant component (ca. 80 wt.%) of the reaction mixture at any conversion rate. Therefore, it is likely that mainly benzene dictates the solubility of water. As a matter of fact, if the calculation of water solubility is carried out with reference to the final reaction compositions, quite similar results are obtained (Table 2), even in the case of test 1, where the lowest IPA conversion and the largest amounts of IPA, DIPE and propylene were present among the products. For the sake of simplicity, in the calculation DIPE is conservatively taken as IPA on a weight basis and minor by-products have been omitted. In the following, water solubility in benzene will be taken as a reliable indication of the water solubility in the reaction system.

It is likely that undissolved water could interact more strongly with the catalyst, killing its activity. According to this view, the reaction would proceed only until water concentration in the reaction mixture reaches the solubility limit at which water forms a separate liquid phase. Then, the stable adsorption of undissolved water onto the catalyst surface would hinder further conversion of IPA and of propylene and DIPE intermediates found in substantial amounts in the final reaction mixture of test 1.

A specific role of undissolved water in creating an upper limit for reaction advancement is supported by considering that the quantity of water formed in both tests 1 and 2 largely exceeded the number of total acid sites available in the catalyst, even assuming that Al content in the zeolite would correspond to total zeolite acid sites (the actual quantity of acid sites determined by pyridine titration is normally lower than Al content in acid zeolites): 0.0048 mol of Al were present in the reaction system (4.0 g of zeolite powder), while the

total formed water amounted to 0.36 mol in test 1 and 0.12 mol in test 2.

Further catalytic experiments were done in order to assess the temperature effect (tests 3 and 4).

At 190 °C (test 4) IPA conversion became comparable to the reference test in Table 1. Also selectivities to both cumene and aromatics increased with temperature in a similar way, mainly due to the disappearance of propylene and DIPE intermediates among the products.

Increasing reaction temperature both specific catalyst activity and water solubility increase. Due to the latter water concentration in tests 3 and 4 became progressively lower than the corresponding water solubility values, removing the above mentioned limit for reaction advancement. At the same time tests 2–4 also suggest that, even when the formed water concentration lies below the solubility value, presence of dissolved water, especially at the highest concentration levels, brings about some decrease in catalyst activity that must be counteracted by a proper temperature increase.

3.2. Continuous catalytic tests

A new set of catalytic tests by using a continuous fixed bed reactor were done first in order to confirm suggestions and interpretations coming out from previous batch catalytic tests and also to evaluate catalyst lifetime, one of the most important performance parameter from the industrial point of view in cumene synthesis.

Continuous tests have all been made with a [benzene]/[IPA] ratio around 6, as this condition is quite close to the industrial cumene production. These tests have been planned based on the driving idea that in order to obtain good catalyst performances—when IPA is used in place of propylene as a benzene alkylating agent—formation of undissolved water should be avoided and water concentration in the liquid phase should be kept low.

A way to realise such conditions is bringing water in vapour phase through a proper selection of reaction temperature and pressure by which a mixed liquid–vapour or full vapour phase state of the reaction mixture can be obtained.

By calculation of the amount of liquid and vapour phase it is possible to get only a rough indication

of the real physical state of the reaction mixture throughout the reaction, since the composition continuously changes heavily affecting the phase state. To carry out the calculation, among all the possible compositions we have chosen, mainly in view of the rather extensive IPA dehydration observed in all reaction conditions, a *composition 1* corresponding to the benzene/propylene/water mixture stoichiometrically equivalent to the starting [benzene]/[IPA] ratio.

Results of continuous tests are shown in Table 3. The first column shows the result of a reference test with propylene. Reported results refer to 5 h time on stream (t.o.s.) sampling.

At 190 °C inlet temperature and 30 bar pressure (test 5), the physical state of the reaction mixture corresponds to a mixed phase state: at a total formed water amounting to 3.0 wt.%, 2.3 wt.% of water concentration in the liquid phase fraction can be calculated.

IPA conversion was approaching the one of the reference test, while selectivities were still considerably lower. Catalyst activity declined just after some hours of time on stream (see later).

In test 6, the reaction pressure was lowered to 19 bar. An enhanced vapour fraction in the mixed phase state of the reaction mixture was so obtained and the formed water concentration in the liquid phase became considerably lower (0.9 wt.%) than in test 5. As a result, selectivities to both cumene and aromatics greatly increased and became close to the reference values. Moreover, the rapid catalyst deactivation experienced in test 5 was not observed.

In test 7, by increasing the inlet temperature to around 210 °C at a 30 bar pressure (the same of test 5), a mixed phase state and a water concentration in liquid phase falling between tests 5 and 6 (1.5 wt.%) were obtained. Catalyst performances remained quite comparable to test 6, with a slightly increased selectivity to aromatics.

In test 8, by decreasing the reaction pressure to 9 bar at the same temperature of test 7, the reaction mixture completely turned to a vapour phase state. Catalyst performances fully comparable to the reference were then observed.

A detailed examination of the formation of minor byproducts gives some further interesting indications, n-propylbenzene and propylene oligomers playing the role of catalyst activity indexes.

Table 3
Continuous catalytic tests

	Reference	No.			
		5	6	7	8
Test conditions					
WHSV[a]	4	4	4	4	4
Alkylating agent	Propylene	IPA	IPA	IPA	IPA
[C6]/[IPA or C3-]	6.2	6.3	6.2	6.2	6.0
Inlet/maximum temperature (°C)	153/176	190/194	188/193	208/212	210/214
Pressure (bar)	37	30	19	30	9
Phase state[b]	Liquid	Mixed	Mixed	Mixed	Vapour
Phase state[c]		Liquid	Mixed	Liquid	Vapour
Results					
Conversion ([IPA or C3-) %	99.5	92.9	99.7	99.7	100.0
Select [cumene]/[IPA or C3-] (%)	88.6	51.1	86.5	86.6	88.6
Select [aromatics]/[IPA or C3-] (%)	99.8	55.0	96.8	97.5	99.3
Total water formed in reaction mixture (wt.%)	–	3.0	3.3	3.3	3.4
Water in liquid phase fraction (wt.%)[b]	–	2.3	0.9	1.5	–
Water in liquid phase fraction (wt.%)[c]	–	3.0	2.3	3.3	–
Calculated water solubility (wt.%)	–	4.3	4.1	6.3	6.3
Products distribution (wt.%)[d]					
Propylene	0.16	20.0	0.91	0.55	0.054
Diisopropylether		1.84	0.007	0.012	0.002
Oligomers	0.024	0.91	0.17	0.27	0.037
Toluene + ethylbenzene	0.001	0.037	0.015	0.021	0.091
n-Propylbenzene	0.026	0.017	0.018	0.026	0.10
Cumene	91.9	73.3	91.4	91.3	92.0
Phenyl-C4	0.022	0.017	0.022	0.019	0.059
Phenyl-C5	0.013	0.007	0.022	0.025	0.076
Diisopropylbenzene	7.56	3.63	6.91	7.39	7.15
Triisopropylbenzene	0.25	0.16	0.36	0.27	0.31
Heavies (>phenyl-C6)	0.080	0.024	0.060	0.033	0.10

[a] Referred to zeolite content.

[b] See text, @ *composition* 1.

[c] See text, @ *composition* 2.

[d] On water free basis, without reactants.

n-Propylbenzene formation is greatly favoured by temperature in the benzene alkylation with propylene [14], given the same catalyst, and a lower *n*-propylbenzene formation is normally recognised as a sign of lower catalyst activity.

n-Propylbenzene formation in tests 5–7 remained lower than or almost comparable to the reference test while in test 8 a considerable increase occurred. The expected increase with temperature in *n*-propylbenzene formation was then observed only in test 8 where a complete vapour phase state of the reaction mixture was present, even if in tests 7 and 8 reaction temperatures were the same. It is then quite clear that only water in the liquid phase, even when its concentration is far away from the solubility limit, has a role in lowering the catalyst activity while, at complete vapour phase state of the reaction mixture and at the same amount of water, catalyst activity seems no longer negatively affected.

Also the increase of propylene oligomers in tests 5–7, compared to the reference test, indicates a lower catalyst activity specifically related to the water concentration in liquid phase, as it is normally recognised that, with the same catalyst, propylene oligomerization is greatly disfavoured by increasing temperature.

Comparing tests 5–8, based on the propylene oligomers index, catalyst activity increases when water concentration in liquid phase decreases. The

propylene oligomers formation became comparable to the reference only in test 8 where water in liquid phase was absent.

It has been shown [15] that propylene oligomers formation in cumene reaction from benzene and propylene catalysed by β-zeolites at liquid phase conditions was higher when β-zeolites with higher SAR were used. Based on the above suggestion the catalyst performances of a β-zeolite-based catalyst in the presence of water would be then comparable, from a qualitative point of view, to the performance of a β-zeolite with higher SAR, due to a certain fraction of catalyst acid sites made unavailable for the reaction, bringing to a net acid sites reduction.

It has to be pointed out that similar conclusions, from a qualitative point of view, would have been reached if a different *composition* 2, e.g. corresponding to the final reaction mixture, would be taken for phase state calculation. The real evolution of the physical state during the reaction advancement is expected to be comprised between the two extreme states calculated by assuming *composition* 1 and *composition* 2.

Test 5, the one with the poorest performances, would result in a complete liquid phase with 3.0 wt.%

of dissolved water. In test 6, showing good results, a mixed phase state of the reaction mixture would be calculated and water concentration in the liquid phase would become considerably lower (2.3 wt.%) than in test 5. For test 8, fully comparable to the reference, a complete vapour phase state would still be predicted as before. The interpretation of test 7, showing an intermediate catalytic behaviour, becomes somewhat more puzzling, since using *composition* 2 it would turn to a liquid phase state, resulting in a water concentration similar to test 5 (3.3 wt.%). Likely, as already observed in discussing the batch tests, a higher reaction temperature helps to bear higher water concentrations through an enhanced specific catalyst activity, besides increasing the water solubility limit (6.3 wt.% versus 4.3 wt.%).

3.3. Catalyst deactivation rate versus water concentration

Fig. 1 shows IPA (or propylene) conversion versus total catalyst productivity during time on stream (cumulative production, kg cumene/kg of catalyst) for the
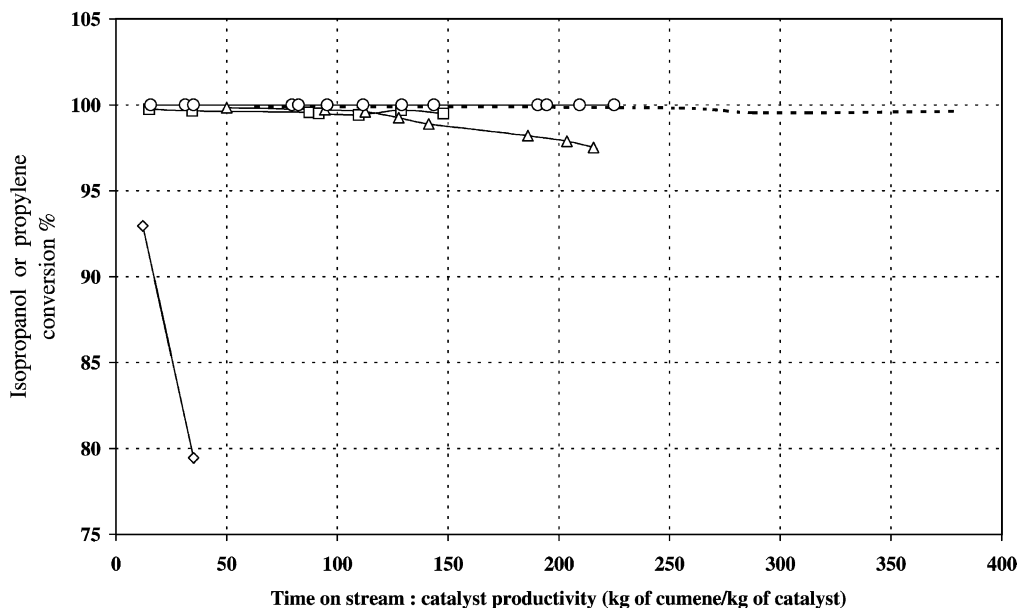

Fig. 1. Benzene alkylation with IPA: IPA or propylene conversion vs. time on stream. Effect of water concentration (wt.% @ *composition* 1) in the liquid phase fraction of the reaction mixture: (◇) test no. 5 (2.3); (□) test no. 6 (0.9); (△) test no. 7 (1.5); (○) test no. 8 (0.0); (---) reference test (0.0). See Table 3 for details on reaction conditions.
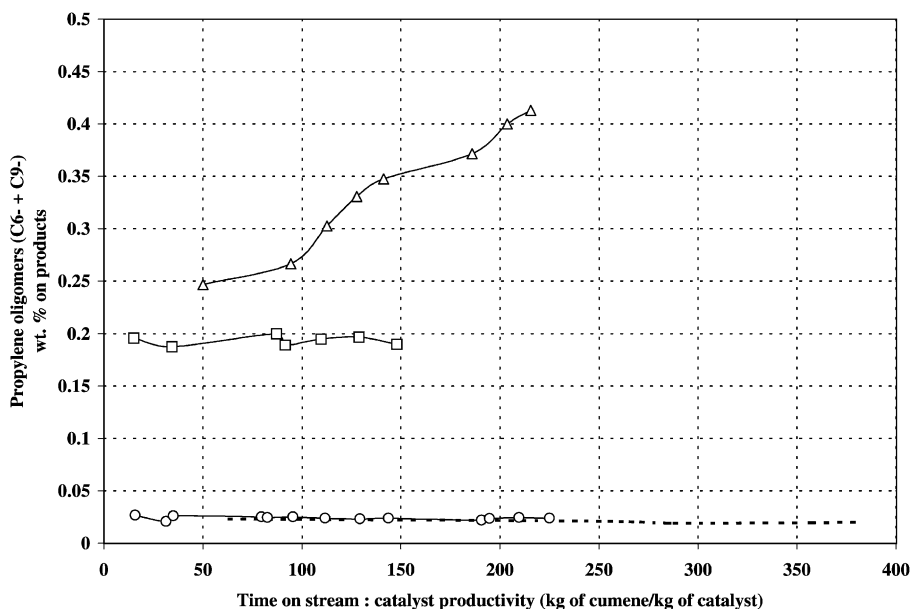
Fig. 2. Benzene alkylation with IPA: propylene oligomers vs. time on stream. Effect of water concentration (wt.% @ *composition* 1) in the liquid phase fraction of the reaction mixture: (□) test no. 6 (0.9); (△) test no. 7 (1.5); (○) test no. 8 (0.0); (---) reference test (0.0). See Table 3 for details on reaction conditions.

five continuous catalytic tests whose results were reported in Table 3.

In test 5, IPA conversion declined just after some hours of time on stream while all the remaining tests showed a quite more stable activity with time on stream. Only test 7, among the group of tests 6–8, showed some deactivation, according to the highest water concentration in liquid phase which would lead to the highest effect in decreasing catalyst activity.

The catalyst activity reduction due to water leads to an increase in free propylene concentration favouring the formation of propylene oligomers [15] which are in turn coke precursors [16]. Deactivation rate in tests 5 and 7 would then depend on a higher coke precursor formation. Propylene oligomers formation versus time on stream for tests 6–8 and for reference test is reported in Fig. 2, clearly showing a correlation with the water content in the liquid phase fraction (propylene oligomers versus t.o.s. for test 5 would have largely exceeded the graph scale and is not reported).

As a recognised coke precursor the propylene oligomers fraction in tests 6 and 8, with the lowest amounts of water in the liquid phase, remained almost constant with time on stream while a considerable

increase in test 7 was found during the run, in accordance with the higher catalyst deactivation rate already shown in Fig. 1. Only test 8 shows a propylene oligomers formation as low as the reference test.

A water concentration in the liquid phase fraction of the reaction mixture of 0.88 wt.% (as it was in test 6, calculated using composition 1) can be taken as the upper limit in order to achieve good reaction performances and to avoid catalyst deactivation phenomena [9].The above indication on the tolerable amount of dissolved water would have been obviously different if we had taken *composition 2* as a basis for RKS calculation to define the physical state of the reaction mixture. Therefore, it has to be taken only as a practical tool to predict suitable reaction conditions corresponding to good catalytic performances and low catalyst deactivation rate.

Finally, it deserves to be remarked that, based on the present results, vapour phase reaction conditions stem out as the best suited for benzene alkylation with IPA while, in the case of propylene, liquid phase conditions are the preferred ones, as a rule, due to a quite higher catalyst deactivation usually experienced in vapour phase.

4. Conclusions

By using the same proprietary β-zeolite-based catalyst used in Polimeri Europa's industrial cumene production technology, direct benzene alkylation to cumene with isopropanol, instead of propylene, has been proven. Under properly selected reaction conditions, able to avoid the negative effect of water on the catalyst, reaction performances as good as those obtained with pure propylene, at comparable [benzene]/[alkylating agent] ratio in the feedstock, can be obtained.

The use of isopropanol as a benzene alkylating agent paves the road toward a viable acetone recycle in cumene/phenol production, as foreseeable in case of acetone/phenol unbalanced market demand.

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