Polymer-Supported Reagents. Part I. Ketalization of Cyclohexanone with Ethylene Glycol by Polymer-Supported Diphenylamine-Titanium Tetrachloride Complex. A Kinetic Study

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POLYMER-SUPPORTED REAGENTS. PART I. KETALIZATION OF CYCLOHEXANONE WITH ETHYLENE GLYCOL BY POLYMER-SUPPORTED DIPHENYLAMINE–TITANIUM TETRACHLORIDE COMPLEX. A KINETIC STUDY

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ABSTRACT

Insoluble microporous polystyrene-bound diphenylamine–titanium tetrachloride complex has been used as a catalyst in the ketalization of cyclohexanone with ethylene glycol. The kinetics of the reaction was studied, and a suitable mechanism was proposed based on the results obtained. The observed reaction rates depend on many experimental parameters, viz., stirring speed, concentration of cyclohexanone and ethylene glycol, temperature, percent active site (percentage of ring substitution), and percent crosslinking of the polymer. The rates were found to increase on increasing the stirring speed from 0 to 500 rpm and then decrease from 500 to 800 rpm. The rate of ketalization increases with increasing concentration of ethylene glycol, catalyst amount, and temperature, and decreases with increasing concentration of cyclohexanone and percentage crosslinking of the polymer.

INTRODUCTION

Attachment of a homogeneous catalyst to an insoluble polymer has the potential of conferring on such catalysts certain special advantages not available in simple homogeneous catalysts. Organic macromolecules can often act as ligands for transition metal complexes, thus affecting the structure and catalytic properties of the systems rather than inert supports for heterogenizing soluble complexes.

Both crosslinked and linear organic and inorganic polymers have been largely used in the last two decades for heterogenizing transition metal catalysts. These supports can be functionalized to give ligands for attaching transition metal complexes through coordinate bonds as in the corresponding soluble monomer analogs. The advantage of this approach is to prepare catalysts displaying good activity, selectivity, and reproducibility typical of homogeneous catalysts, combined with the easy separability and recovery characteristics of heterogeneous catalysts [1–3].

Polymeric catalysts consisting polystyrene with Lewis acids such as $AlCl_3$, BF_3, and $TiCl_4$ have been used in organic synthetic reactions such as esterification, acetalation, ketal formation, etherification, and Friedel-Crafts alkylation [4–8]. However, no kinetic investigation has been made using polymer-supported Lewis acid catalysts. We report here the kinetics of ketalization of cyclohexanone with ethylene glycol in ethyl acetate solvent medium, using insoluble microporous polystyrene-bound diphenylamine–titanium tetrachloride as a catalyst.

EXPERIMENTAL

Materials

Styrene (Fluka), *p*-methylstyrene (Fluka), DVB (Polysciences, I.C.P.A), polyvinyl alcohol (Fluka), gelatin (AR, BDH), diphenylamine (AR, Qualigens), and titanium tetrachloride (Johnson Matthey Alfa Products) were used as such in the polymer preparation. AIBN (Kochlight, USA) was recrystallized from ethanol. Cyclohexanone (AR, SDS), ethylene glycol (AR, SDS), and ethyl acetate (AR, Fischer) were distilled before use. The reaction mixtures were stirred by a mechanical stirrer (Tullu FHP motor, UP National Mfrs. P. Ltd). Stirring speed was measured using a tachometer (Teclock, Japan). GC analyses were performed on a Varian 3700 with a Vista CDS 401 data system having a flame ionization detector with a 3 m × 1/8 inch column of 10% SE-30 on 80–100 chrom WHP.

Synthesis of Benzyldiphenylamine and Benzyldiphenylamine–Titanium Tetrachloride Complex

Equimolar quantities of diphenylamine (0.2 mol) and benzylchloride (0.2 mol) were heated at 100–105°C for 10 hours with anhydrous sodium acetate (15 g) and 0.5% iodine on the weight of diphenylamine taken [9]. The mass was then poured into 20% hydrochloric acid and the solution cooled with ice and allowed to stand for 2 hours. The condensation product was washed with 70% methanol and recrystallized with 70% hot methanol (mp 88°C, lit. 88–88.5°C).

Benzyldiphenylamine (20 g, 77 mmol) was dissolved in 100 mL chloroform, and 15 mL titanium tetrachloride was added. The mixture was stirred for 30 minutes

at room temperature. The benzyldiphenylamine–titanium tetrachloride complex (BDA–TiCl$_4$) was filtered under vacuum and washed with an excess of chloroform. The complex (hygroscopic, containing 31.60% of chloride ion) was stored under a vacuum dessicator.

Synthesis of the Crosslinked Poly(p-Chloromethyl)styrene

Copolymers of styrene and p-methylstyrene, crosslinked with divinylbenzene, were prepared by the suspension copolymerization technique [10]. Polymers with different percentages of crosslinking, 2–10% by weight of DVB, and different percent active sites, viz., 25, 50, and 75% by weight of p-methylstyrene, were prepared. The crosslinked poly(p-methyl)styrene was chlorinated using sulfuryl chloride as a chlorinating agent and AIBN as a free-radical initiator in benzene medium [11]. The chloromethylated crosslinked polystyrenes are key intermediates in the preparation of triphase catalysts [12], supports for solid-phase peptide synthesis [13, 14], and supports for polymeric carriers, reagents, and catalysts [1, 8, 15–19].

The chlorinated polymers were converted to quaternary ammonium ions (polymer-supported phase-transfer catalysts) by the method of Ford et al. [18], using triethylamine as the quarternizing agent. The chloride ion concentrations were estimated by a modified Volhard titration method. According to the chloride contents, the polymers have 15–18, 32–34, and 55–58% degrees of chlorination in the original copolymers having 25, 50, and 75% vinyltoluene, respectively.

Synthesis of the Polymer Supported Diphenylamine–Titanium Tetrachloride Complex

Chloromethylated crosslinked polystyrene beads (20 g) swollen in 100 mL chloroform were added to 200 mL of a chloroform solution of diphenylamine (25 g, 148 mmol) [8]. The above mixture was stirred for 18 hours at 50 ± 0.2°C, pyridine (10 mL) was added to the mixture, and then stirred for 2 hours. The polymer beads were filtered and washed successively with THF, double distilled water, and acetone. The polymer beads were dried under vacuum at 50°C for 2 days.

The diphenylamine-anchored polymer beads (15 g) were swelled in chloroform, and 10 mL TiCl$_4$ was added [8]. The mixture was stirred for 8 hours at room temperature and then cooled (0–10°C). The beads were filtered and then washed with chloroform and acetone. The catalyst was further dried under vacuum at 50°C for 2 days.

The steps involved in the preparation of polymer-supported diphenylamine-titanium tetrachloride are given in Scheme 1.

The observed percentages of composition of the elements present in the 2% crosslinked, 50% ring-substituted polymeric titanium tetrachloride catalyst are %C 66.45, %H 6.60, %N 1.43 (calculated: %C 69.12, %H 7.27, %N 1.98).

IR Spectral Analysis

The obvious difference between the IR (Perkin-Elmer 598 Spectrophotometer) spectra of polymeric benzyldiphenylamine–titanium tetrachloride complex (PS-BDA–TiCl$_4$) and polymeric benzyldiphenylamine (PSBDA) were at 2800–3500
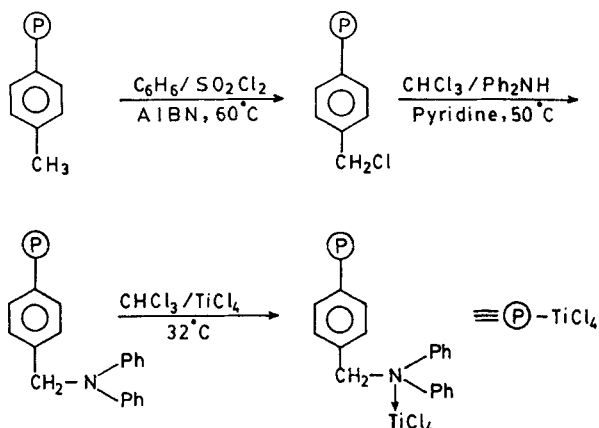
SCHEME 1.

cm^{-1}, at 600–800 cm^{-1}, and a characteristic absorption band showed at 1350 cm^{-1} for tertiary amine. The intensity of this band decreases for the PSBDA–TiCl$_4$ complex. For this reason, the polymeric titanium tetrachloride complex is very stable and shows good catalytic activity.

The catalyst was sieved into different particle sizes, viz., $-40+60$, $-60+80$, $-80+120$, $-120+170$, $-170+200$, and -200 mesh (US standard). The chloride ion concentrations were estimated according to the oxygen flask method [20, 21] and were found to be 1.19, 3.689, and 4.403 milliequivalents of chloride per gram of catalyst for 25, 50, and 75% active sites, respectively.

Typical Kinetic Experiment

A 150-mL three-necked round-bottomed flask was charged with 30 mL ethyl acetate, 50 mmol cyclohexanone, and 50 mmol ethylene glycol. The flask was placed in a thermostat maintained at 50 ± 0.2°C and stirred mechanically with a 45 × 18 mm curved Teflon blade at 500 rpm for 10 minutes to condition the substrates. Before adding the catalyst, sample was drawn from the reaction mixture. 0.1 g of 2% crosslinked, $-40+60$ mesh, 50% active site catalyst was added to the reaction mixture. The samples were collected at regular intervals and analyzed using GC. The amount of cyclohexanone that disappeared from the reaction mixture was estimated, and the second-order rate constants were calculated from plots of $1/(a - x)$ vs time, where $(a - x)$ is the concentrations of cyclohexanone at a given time t.

RESULTS AND DISCUSSION

The kinetics of ketalization of cyclohexanone with ethylene glycol using polymer-supported titanium tetrachloride catalyst (Ⓟ —TiCl$_4$) was conducted in an excess of solvent (ethyl acetate, 306 mmol) and a small amount of cyclohexanone and ethylene glycol (50 mmol each). Catalyst (50–400 mg) was added to the above

system. The reaction system obeyed second-order kinetics, and the rate constants were calculated. In our experimental conditions there was no transesterification observed between ethylene glycol and ethyl acetate.

Effect of Stirring Speed on Conversion

The effect of stirring speed on the rate of the reaction was studied by varying the stirring speed from 0 to 800 rpm. The reaction rate was found to increase with increasing stirring speed from 0 to 500 rpm, and then decreased from 500 to 800 rpm (Table 1). This indicates that the mass transfer of reactants from bulk liquid to the surface of the catalyst is not a factor that limits the reaction rate throughout the rpm's studied. When the mixture is stirred mechanically, an increase in reaction rate is observed, which is due to the promotion of contact between catalyst and substrates, thereby making more substrates react, so the reaction is under mass transfer control (100–500 rpm) [18]. When the stirring speed is increased beyond a certain limit, typically 500 rpm in the present study, the maximum possible concentrations of reactants at the catalyst–particle surface are minimized, and so the entrance of substrates into polymeric beads is prohibited, unlike in conditions at slower stirring speeds. Hence the reaction rate is decreased (500–800 rpm).

Effect of Catalyst Amount and [Substrate]

The effect of catalyst and substrate amounts on the rate of reaction was studied by varying the catalyst amount from 50 to 400 mg and also varying the amounts of cyclohexanone and ethylene glycol from 10 to 90 mmol and 30 to 110 mmol, respectively. In the absence of catalyst, no reaction takes place. The second-order rate constant increases linearly with the amount of catalyst (Fig. 2). The increased rate with added catalyst amount indicates that the rate-limiting step of the reaction may take place within or on the surface of the catalyst [22].

TABLE 1.   Effect of Stirring Speed on Rate Constant for the Reaction with 2% Crosslinked, $-40+60$ Mesh, 50% Active Site Catalyst at 50°C

Stirring speed, rpm	$k_2 \times 10^5$ $M^{-1} \cdot min^{-1}$
0	3.7111
100	5.0825
200	6.8665
300	7.9917
400	8.1167
500	16.0865
600	8.5263
700	7.5282
800	7.4664

The rate constant (k_2) was found to increase on increasing the amount of ethylene glycol. On the contrary, an increase in the concentration of cyclohexanone decreased the rate constant (Fig. 1). We believe that two types of complexes are possible between the polymeric titanium tetrachloride, ethylene glycol, and cyclohexanone (Scheme 2). Both complexes give the same product on decomposition, namely 2,2-pentamethylene-1,3-dioxolane. The complex formation has been verified by taking the UV spectrum of individual compounds after mixing them in a 1:1 molar ratio. When the concentration of cyclohexanone increases, formation of the ternary complex (a) in Scheme 2 is favorable, which will passivate the Lewis site of the titanium center, and a decrease of the rate constant is observed. In sharp contrast, an increase of the concentration of ethylene glycol formation of ternary complex (b) in Scheme 2 is favorable, which will activate product formation.

Effect of Degree of Crosslinking and Ring Substitution

The rate of formation of 2,2-pentamethylene-1,3-dioxolane increases with a decrease in the percentage crosslinking of the polymer (Fig. 2). The degree of
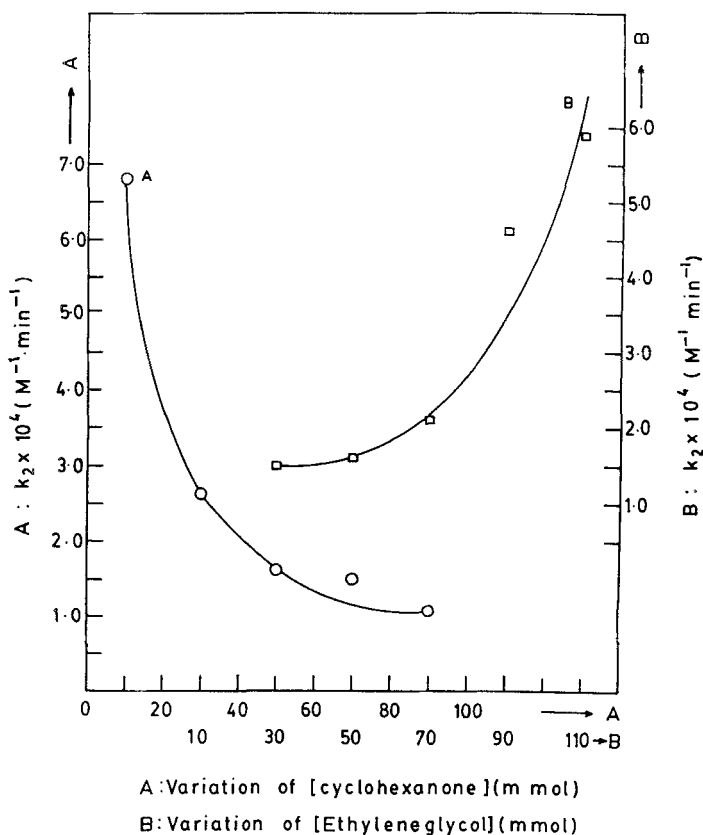

A :Variation of [cyclohexanone](m mol)
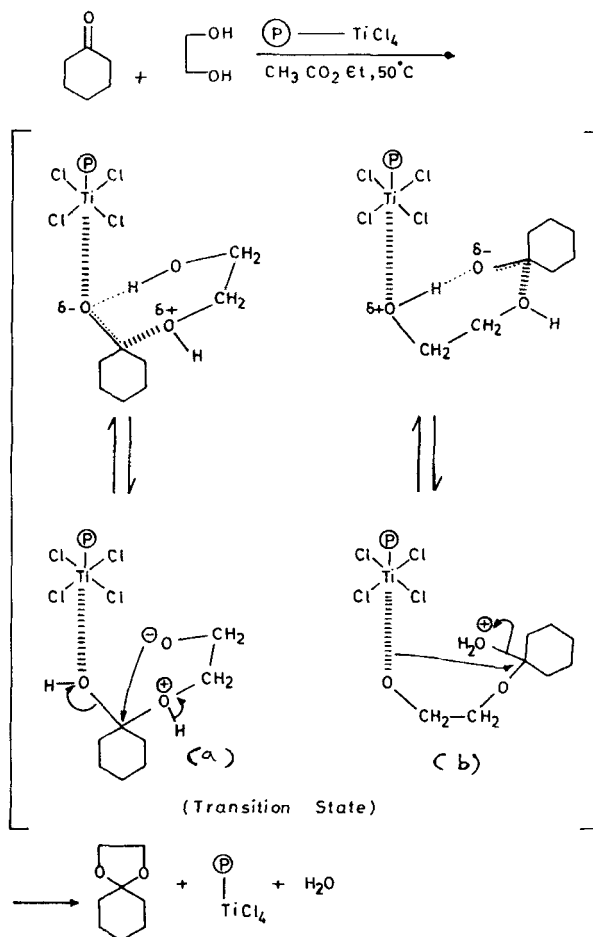
B :Variation of [Ethyleneglycol](mmol)

FIG. 1.   Effect of [cyclohexanone] (Curve A) and [ethylene glycol] (Curve B) on the rate of the reaction with 2% crosslinked, $-40+60$ mesh, 50% active site catalyst at 500 rpm and 50°C. Curve A: $k_2 \times 10^4$ $(M^{-1} \cdot min^{-1})$ vs [cyclohexanone (mmol)]. Curve B: $k_2 \times 10^4$ $(M^{-1} \cdot min^{-1})$ vs [ethylene glycol (mmol)].

SCHEME 2.

crosslinking controls the diffusion rates by controlling the swelling of the polymer matrix [23].

Table 2 shows the rate of formation of ketal with an increased percentage of active sites of the polymer-supported catalyst. The catalytic activity increases with an increase in the percent active site from 25 to 50% and decreases with a further increase in the percent active site from 50 to 75%.

The increased activity with an increase in the percent active site from 25 to 50% may be attributed to increased swelling of the catalyst. Therefore, the intraparticle diffusion and intrinsic reactivity also increase [24, 25], and so the rate of formation of the product is higher. The decrease in reactivity from 50 to 75% active site is because of the slower diffusion of the reactants into the catalyst particle, since swelling of the catalyst decreases with the number of functional groups in the polymer matrix [26].
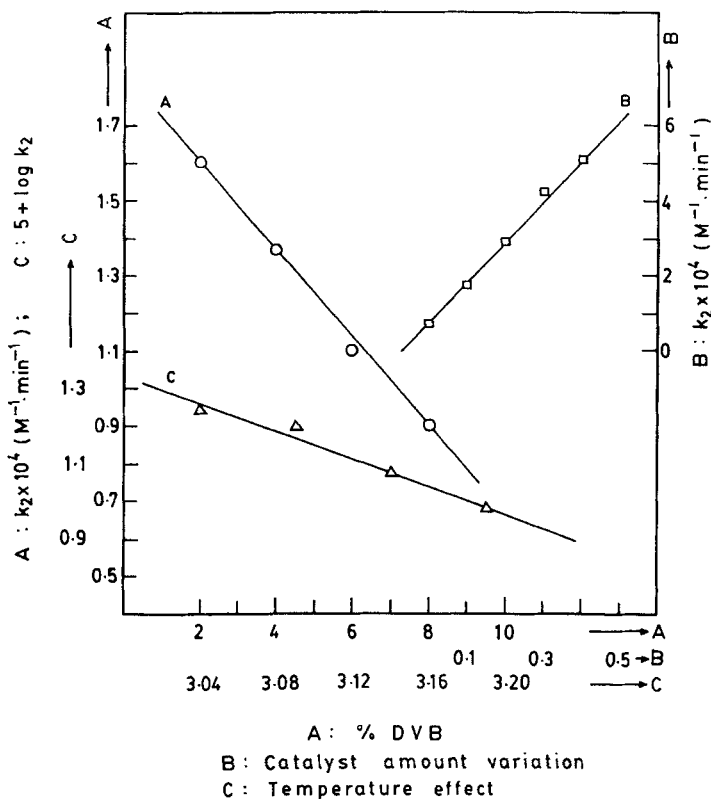
FIG. 2.   Curves A, B, and C are percent crosslinking, catalyst amount, and temperature effect on rate constant of 50% active site, $-40+60$ mesh at 500 rpm, respectively. Curve A: $k_2 \times 10^4$ ($M^{-1} \cdot min^{-1}$) vs %DVB. Curve B: $k_2 \times 10^4$ ($M^{-1} \cdot min^{-1}$) vs [catalyst amount (g)]. Curve C: $5 + \log k_2$ vs $1/T$ (deg^{-1}).

Swelling of Catalyst

Dry catalyst (2% crosslinked, $-40+60$ mesh, 50% active site), 2.0 mL, was placed in a graduated centrifuge tube which had been heated to 50°C, and 15 mL of ethyl acetate at 50°C was added, stirred, and allowed to stand. The catalyst volume increased to 3.6 mL in 5 minutes. The above experiment was repeated with the

TABLE 2.   Effect of Percent Active Site on the Rate of the Reaction with 2% Crosslinked, $-40+60$ Mesh Catalyst at 500 rpm and 50°C

Percent of active site	$k_2 \times 10^4\ M^{-1} \cdot min^{-1}$
25	0.4681
50	1.6087
75	0.8034

substrates instead of ethyl acetate. The catalyst was allowed to swell in the respective substrates. The catalyst volume increased to 3.1 and 3.4 mL in 5 minutes for 10 mL cyclohexanone and ethylene glycol, respectively. The increased volume did not change even after 15 hours in all these experiments.

Control Experiments

Reactions were carried out with 0.5 g of 2% crosslinked 50% active site chloromethylated polystyrene, diphenylamine-anchored polystyrene, and without catalyst. Less than 2% ketalization of cyclohexanone occurred in 1 hour in all cases.

The ketalization reactions were also carried out with 3.689 milliequivalents of titanium tetrachoride and benzyldiphenylamine–titanium tetrachloride complex. The reaction rates observed were 50 and 4 times faster as compared with the polymeric titanium tetrachloride catalyst, respectively. In these homogeneous conditions the rates of formation of ketal do not change with varying stirring speeds from 200 to 600 rpm. However, in the polymeric catalyst the rate of formation of product considerably changes with a change of stirring speed (Table 1).

The polymeric titanium tetrachloride complex could easily be recovered from the reaction mixture by filtration, and it was reused three times without any discernible change of activity. After three times the rate of formation of ketal decreases, which may be due to leaching out of titanium tetrachloride from the polymeric carrier. The original activity of the catalyst could be regained after 6 hours by adding titanium tetrachloride to the polymeric carrier in chloroform at room temperature.

Temperature Effect

Rates of ketalization of cyclohexanone with ethylene glycol were determined using 2% crosslinked, $-40 + 60$ mesh, 50% active site catalyst at four different temperatures: 40, 45, 50, and 55°C. An Arrhenius plot of k_2 vs $1/T$ is given in Fig. 2. The activation parameters were evaluated from Arrhenius plots (Table 3).

The Arrhenius parameters were calculated in the 45–50°C range under homogeneous condition (using BDA–TiCl$_4$) (Table 3). The activation parameters do not differ much from those of the supported system. This suggests that preorganization is not required for the reaction to occur. The rate is 4 times as fast as that of the polymeric catalyst.

TABLE 3. Activation Parameters for the Reaction with BDA–TiCl$_4$ and PSBDA–TiCl$_4$ Catalyst at 500 rpm

Catalyst	E_a, kJ·mol^{-1}	$\Delta H\ddagger$, kJ·mol^{-1}	$\Delta S\ddagger$, eu	$\Delta G\ddagger$, kJ·mol^{-1}
BDA–TiCl$_4$	35.8	33.1	-192.7	85.4
PSBDA–TiCl$_4$	35.8	33.2	-179.1	91.0

Reaction Mechanism

The rates of the reactions catalyzed by insoluble polymer supported catalysts are limited by the following factors [22].

1. Mass transfer of the reactants from the bulk solution to the exterior surface of the catalyst particle.
2. Diffusion of the reactants from the surface to the active catalytic site.
3. The catalytic reaction itself.
4. Diffusion of the products away from the active site to the catalyst particle surface.
5. Mass transfer of the products from the surface into the bulk solution.

The rate-limiting step of the ketalization reaction must take place within or on the surface of the polymer because ketalization of cyclohexanone increases linearly with the amount of added catalyst.

A higher E_a and a higher negative $\Delta S\ddagger$ value indicate that the catalyst, cyclohexanone, and ethylene glycol must form a transition state as the rate-determining step. No other products were detected by gas–liquid chromatography. Therefore, no bond is broken between carbon and oxygen in ethylene glycol [6].

From the observed experimental results, the mechanism of Scheme 2 is proposed.

CONCLUSIONS

Because the polymer-supported titanium tetrachloride complex is insoluble, it is easily recoverable, reusable, recyclable, noncorrosive, has good stability, and also has good catalytic activity for the ketalization and esterification [27] reactions. Thus it can be considered a potential catalyst for industrial orientation.

ACKNOWLEDGMENT

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